INVESTIGATION OF DIFFERENT DEGRADATION METHODS TO PREPARE LIQUID EPOXIDIZED NATURAL RUBBER FOR COATING APPLICATIONS

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ABSTRACT

Epoxidized natural rubber (ENR) is a very significant polymer due to its outstanding mechanical performance besides low cost and great mechanical properties. However, ENR has high molecular weight which limits its solubility and its processability. This study concerns the degradation of ENR to shorter chain lengths to form liquid epoxidized natural rubber (LENR) employing 5 different methods, i.e. (i) mechanical milling, (ii) chemical degradation initiated by potassium peroxodisulfate, (iii) photo-oxidation initiated by ultra violet (UV), (iv) oxidative degradation by periodic acid (H_5IO_6) and (v) oxidative degradation by potassium permanganate ($KMnO_4$). The first three methods [(i), (ii) and (iii)] break-down of ENR is via free radicals, but at different rates and mechanisms. FTIR and NMR results showed that in these three methods ketone, aldehyde, carboxylic acid, ester and lactone groups were observed; however only during the UV degradation a hydrofuranic structure was formed. The oxirane group was not affected significantly during the degradation, indicating that the chain scissions had occurred predominantly via the double bonds. Comparison of the NMR and FTIR spectra of degradation products showed that UV degradation induced more carbonyl and hydroxyl groups to the backbone of the ENR. Increasing of oxygen concentration did not enhance the efficiency in UV degradation method. Mastication with two roll mill produced LENR with greatest degree of unsaturation and less amounts of polar groups. The last two methods [(iv) and (v)] degraded ENR through chemical oxidative degradation. The products of these two methods were compared with LENR obtained from degradation initiated by UV irradiation. Degradation of ENR by $KMnO_4$ and UV irradiation proceeded mostly by attack via double bond, as confirmed by NMR

spectroscopy irradiation proceeded mostly by attack via double bond, as confirmed by NMR spectroscopy whereby a decrease in the ratio peak areas of epoxy methine proton to olefinic methine proton was observed. At concentration of above 0.044 mol H_5IO_6 per hundred grams of rubber (mphr), degradation occurred by ring opening of the oxirane group as confirmed by the NMR of the LENR which showed an increase in the ratio peak areas of olefinic methine proton to epoxy methine proton. The LENR obtained by H_5IO_6 has more ketone groups while the LENR from degradation by $KMnO_4$ has more ester groups. Cyclization of isoprene unit was only observed during the degradation by H_5IO_6. Among these methods, H_5IO_6 has achieved the fastest rate of degradation and lowest M_n under comparable conditions. For coating application, methyl methacrylate (MMA) was graft copolymerized onto LENR using UV radiation and benzophenone as photo initiator. The best grafting efficiency was observed by 0.84 parts per hundred resin (phr) of benzophenone. DSC thermograms showed a small positive shift in T_g of LENR compared to ENR 25. LENR-graft-PMMA showed a great increase in T_g (42ºC), because incorporation of hard segments of PMMA onto LENR. The obtained PMMA-*graft*-LENR was cured with three different amines and evaluated as coatings materials. Overall, the best results for coating performances were observed by curing of PMMA-*graft*-LENR with a cycloaliphatic amine. This type of coating demonstrated the best hardness, adhesion, water and salt resistances.

ABSTRAK

Getah asli epoksida (ENR) adalah polimer yang sangat penting kerana prestasi mekanikalnya yang cemerlang disamping kos rendah dan sifat mekanikal yang hebat. Walau bagaimanapun, ENR mempunyai berat molekul tinggi yang menghadkan kelarutan dan pempropesannya. Kajian ini adalah mengenai degradasi ENR ke panjang rantai yang lebih pendek untuk membentuk cecair getah asli epoksida (LENR) menggunakan 5 kaedah yang berbeza, iaitu (i) pengilangan mekanikal, (ii) degradasi kimia yang dimulakan oleh kalium peroksodisulfat, (iii) foto-pengoksidaan yang dimulakan oleh ultra ungu (UV), (iv) degradasi pengoksidaan oleh asid periodik (H_5IO_6) dan (v) degradasi pengoksidaan oleh kalium permanganat ($KMnO_4$). Tiga kaedah yang pertama [(i), (ii) dan (iii)] bagi pemecahan ENR adalah melalui radikal bebas tetapi pada kadar dan mekanisme yang berlainan. Keputusan FTIR dan NMR menunjukkan bahawa dalam ketiga-tiga kaedah ini kumpulan keton, aldehid, asid karboksilik, ester dan lakton diperhatikan; bagaimanapun hanya semasa degradasi UV struktur hidrofuranik telah dihasilkan. Kumpulan oksirana tidak terjejas dengan ketara semasa degradasi, menunjukkan bahawa pemotongan rantai telah berlaku sebahagian besarnya melalui ikatan dubel. Perbandingan spektra NMR dan FTIR bagi hasil terdegradasi menunjukkan degradasi UV mengaruh lebih banyak kumpulan karbonil dan hidroksil pada rangka ENR. Penambahan kepekatan oksigen tidak meningkatkan kecekapan dalam kaedah degradasi UV. Pengunyahan dengan “two roll mill” telah menghasilkan LENR dengan darjah ketaktepuan terbanyak dan kurang bilangan kumpulan kutub. Dua kaedah terakhir bagi degradasi ENR [(iv) and (v)] adalah melalui degradasi pengoksidaan kimia. Hasil daripada kedua-dua kaedah ini dibandingkan dengan

LENR yang diperolehi daripada degradasi yang dimulakan oleh sinaran UV. Degradasi ENR oleh $KMnO_4$ dan sinaran UV berlaku kebanyakannya oleh serangan melalui ikatan ganda dua, seperti yang disahkan oleh spektroskopi NMR, dimana pengurangan dalam nisbah puncak keluasan proton metin epoksi kepada proton metin olefinik diperhatikan. Pada kepekatan H_5IO_6 melebihi 0.044 mol bagi setiap seratus gram getah (mphr), degradasi berlaku melalui pembukaan gelang kumpulan oksirana seperti disahkan oleh NMR bagi LENR yang menunjukkan peningkatan dalam nisbah keluasan puncak proton metin olefinik kepada proton metin epoksi. LENR yang diperolehi oleh H_5IO_6 mempunyai lebih kumpulan keton manakala degradasi oleh $KMnO_4$ mempunyai lebih kumpulan ester. Pensiklikan unit isoprena hanya diperhatikan semasa degradasi oleh H_5IO_6. Antara kaedah-kaedah ini, H_5IO_6 telah mencapai kadar degradasi yang terpantas dan M_n terendah pada keadaan yang setanding. Bagi aplikasi salutan, metil metakrilat (MMA) telah dikopolimer cantumkan ke LENR menggunakan sinaran UV dan benzofenon sebagai foto pemula. Kecekapan cantuman terbaik diperhatikan melalui 0.84 bahagian per seratus resin (phr) benzofenon. Termogram DSC menunjukkan anjakan positif yang kecil dalam T_g bagi LENR berbanding ENR 25. LENR-cantum-PMMA menunjukkan peningkatan besar dalam T_g (42ºC), disebabkan kemasukan segmen keras PMMA kepada LENR. PMMA-cantum-LENR yang diperolehi telah dimatangkan dengan tiga amina yang berbeza dan dinilai sebagai bahan salutan. Secara keseluruhan, hasil yang terbaik untuk prestasi salutan telah diperhatikan dengan mematangkan PMMA-cantum-LENR dengan amina sikloalifatik. Salutan jenis ini menunjukkan kekerasan, lekatan, serta rintangan air dan garam yang terbaik.

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This thesis is dedicated to my father, Mahdi who passed away on July 30, 2016.

TABLE OF CONTENTS

1 CHAPTER 1: INTRODUCTION XIX

1.1 Research background 1

1.2 Problem statement 4

1.3 Objectives 5

2 CHAPTER 2: LITERATURE REVIEW 6

2.1 Natural rubber 6

2.2 Modification of Natural rubber 8

2.2.1 Physical modification 8

2.2.2 Chemical modification 10

2.3 Epoxidized natural rubber 15

2.4 Liquid natural rubber and liquid epoxidized natural rubber 19

2.4.1 Synthesis 20

2.5 Graft polymerization 35

2.6 Coating 38

2.6.1 General information 38

2.6.2 Epoxy resin 41

3 CHAPTER 3: MATERIALS & METHODS 45

3.1 Materials 45

3.1.1 Preparation of ENR 25 solution 45

3.2 Different degradation methods to produce LENR 46

3.2.1 Mechanical breakdown of ENR25 46

3.2.2 Oxidative degradation initiated by potassium peroxodisulfate. 46

3.2.3 Photo-oxidation with UV radiation. 47

3.2.4 Oxidative degradation with potassium permanganate 48

3.2.5 Oxidative degradation with periodic acid 49

3.3 Graft polymerization 50

3.4 Characterization Methods 51

3.4.1 ^{1}H-NMR spectroscopy 51

3.4.2 FTIR spectroscopy 51

3.4.3 Gel Permeation Chromatography (GPC) analysis 52

3.4.4 Differential scanning calorimetry (DSC) analysis 52

3.4.5 Determination of Epoxy content by direct titration method 53

3.5 Preparation of coating based on grafted LENR 54

3.5.1 Grafted LENR 54

3.5.2 Curing agent 55

3.5.3 Treatment of iron panel 56

3.5.4 Preparation of coating mixture 56

3.5.5 Determination of film properties 57

4 CHAPTER 4: RESULTS AND DISCUSSION 60

4.1 Study of three degradation methods to produce LENR through radical mechanism 60

4.1.1 Introduction 60

4.1.2 Degradation using a roll mill 60

4.1.3 Degradation using potassium peroxodisulfate 65

4.1.4 UV degradation method A 70

4.1.5 Comparison of the three methods 78

4.2 Preparation of LENR by oxidative degradation methods using H_5IO_6 and $KMnO_4$ and comparing them with UV degradation 90

4.2.1 Introduction 90

4.2.2 Degradation by periodic acid 90

4.2.3 Degradation using potassium permanganate 96

4.2.4 UV degradation method B 100

4.2.5 Comparison of the three methods 103

4.3 Preparation of coating based on LENR 110

5 CHAPTER 5: CONCLUSION AND FURTHER WORK 121

5.1 Conclusions 121

5.2 Suggestion for further research 124

6 REFERENCES 126

7 LIST OF ISI PUBLICATIONS AND PRESENTATIONS 136

LIST OF FIGURES

Figure 2.1: Chlorination of NR: (1 Addition reaction. (2 Substitution reaction. 14

Figure 2.2: Hydrogenation of NR using p-TSH at 135 ºC. 15

Figure 2.3: Formation of five- membered cyclic ethers by ring opening of oxirane group. 18

Figure 2.4: Incorporation of dibutyl phosphate to ENR by ring opening of epoxide. ... 19

Figure 2.5: Synthesis of LNR using phenylhydrazine and oxygen as reducing and oxidizing agent 22

Figure 2.6: Scheme of abstraction of allylic hydrogen directly by oxygen molecule. .. 26

Figure 2.7: Different allyl radicals could be generated by radical attack. 26

Figure 2.8: Homolytic decompositon of hydroperoxide to generate ketone..... 27

Figure 2.9: Formation of alkoxy peroxide through subtitution mechanism. 27

Figure 2.10: Formation of alkoxy peroxide by addition mechanism. 28

Figure 2.11: Two-step mechanism for cleavage of the doublebond by H_5IO_6. 31

Figure 2.12: Chemical stucture of DGBA epoxy resin. 41

Figure 2.13: Chemical structure of bisphenol A based epoxy resin. 42

Figure 3.1: Pencil hardness kit 59

Figure 4.1: (a) Changes in subtracted IR spectra in the carbonyl vibration region after 3 & 8 h mastication; (b) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}). 62

Figure 4.2: Changes in subtracted IR spectra in the region of 2962 cm^{-1} in different degradation methods. (a) mastication; (b) degradation with $K_2S_2O_8$; (c) degradation with UV. 62

Figure 4.3: ^{1}H- NMR of (a) ENR25; (b) LENR produced after 8 h mastication. 64

Figure 4.4: Ratio of integration area of the signals at 5.1 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton). 65

Figure 4.5: (a) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}) after 15 and 30 h reaction with $K_2S_2O_8$; (b) Changes in subtracted IR spectra in the 1000 -1150 cm^{-1} region. 66

Figure 4.6: (a) Changes in subtracted IR spectra in the carbonyl vibration region after 15 and 30 h reaction with $K_2S_2O_8$; (b) Changes in subtracted IR spectra in the hydroxyl vibration region. 67

Figure 4.7: Ratio of integration area of the signals at 5.1ppm. (olefinic methine proton) and 2.7 ppm (epoxy methine proton). after reaction with $K_2S_2O_8$. 69

Figure 4.8: ^{1}H-NMR of (a) epoxidized natural rubber; (b) LENR after 30 h reaction with potassium peroxodisulfate 69

Figure 4.9: (a) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}); (b) ratio of A_{835}/A_{2962} of degraded ENR during UV irradiation. 71

Figure 4.10: (a) Changes in subtracted IR spectra in the 1000 – 1150 cm^{-1} region; (b) ratio of absorption of different group to C-H stretching of methyl group at 2962 cm^{-1}. 72

Figure 4.11: (a) Changes in subtracted IR spectra in the carbonyl vibration region; (b) ratio of absorption of different carbonyl group to C-H stretching of methyl group. 72

Figure 4.12: (a) Changes in subtracted IR spectra in the hydroxyl vibration. region; (b) the ratio of peaks at 3358 and 3438 cm^{-1} to C-H stretching of methyl group at 2962 cm^{-1} 73

Figure 4.13: (a) ^{1}H–NMR of hydrofuranic structure; (b) degraded ENR25 and splitting pattern of H_i (m, 1.83 ppm) and H_g (m, 3.73 ppm). 74

Figure 4.14: ^{1}H-NMR spectrum of degraded epoxidized natural rubber after 8 h UV irradiation. 75

Figure 4.15: Decreasing of double bond intensity during photo oxidation calculated by comparing of integration area of the signals at 5.14 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton). 75

Figure 4.16: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in double bond region (=C-H 835 cm^{-1}) 76

Figure 4.17: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in the carbonyl vibration region.....77

Figure 4.18: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in hydroxyl region.....77

Figure 4.19: Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}). A comparison of three degradation methods ; (b) ratio of A_{835}/A_{2962} of different degradation methods. 79

Figure 4.20: (a) Changes in subtracted IR spectra in the carbonyl vibration region. A comparison of three degradation methods; (b) ratio of A_{1717}/A_{2962} of different degradation methods. 80

Figure 4.21: Changes in subtracted IR spectra in the hydroxyl region. A comparison of three degradation methods. 80

Figure 4.22: (a) Radical attack to the double bond of ENR 25. This is the main route in UV degradation and degradation with $K_2S_2O_8$; (b) Allylic hydrogen abstraction through radical attack. 83

Figure 4.23: Free radical attacks double bond to produce alkoxy radical which can convert to alcohol (route 1a) or by β cleavage generate ketone (route 2a, 3a, 4a). 84

Figure 4.24: Free radical abstracts allylic hydrogen to produce alkoxy radical which can convert to alcohol (route 1b) or by β cleavages generate unsaturated ketone (route 2b, 3b, 4b) . The main routes are 1b and 4b. 85

Figure 4.25: The weakest bond will be ruptured by applied force.during mastication and generate methylene radicals which ultimately produce unsaturated ketone. 86

Figure 4.26: Proposed plausible mechanism to form hydrofuranic structure.from alkoxy radicals. 87

Figure 4.27: Nourish Ⅰ reaction 87

Figure 4.28: Intramolecular reaction of acyl radicals generated by Nourish I reaction with alkoxy radical adjacent to carbonyl group to produce lactone.....88

Figure 4.29: Intermolecular reaction of acyl radicals to form ester generated by Nourish Ⅰ reaction with alkoxy radical of another molecule. 88

Figure 4.30: A plausible mechanism for aldehyde generation.....89

Figure 4.31: (A) Changes in absorbance of the double bond region (=C-H wagging) after 10 h reaction with various amounts of H_5IO_6: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{870}/A_{2962} of ENR degraded at different concentrations of H_5IO_6.....91

Figure 4.32: Changes in subtracted IR spectra in the region of 2962 cm^{-1} for different degradation methods: (1) Degradation with H_5IO_6; a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; and d, 0.145 mphr. (2) Degradation with $KMnO_4$; a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; and d, 0.145 mphr. (3) Degradation with UV after different irradiation times. 92

Figure 4.33: (A) Changes in absorbance of the carbonyl group after 10 h reaction with various amounts of H_5IO_6 :a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{1717}/A_{2962} of the degraded ENR with different amounts of H_5IO_6.....93

Figure 4.34: (A) Changes in absorbance of the hydroxyl group after 10 h reaction with various amount of H_5IO_6:a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{3452}/A_{2962} of the degraded ENR with different amounts of H_5IO_6.....93

Figure 4.35: ^{1}H-NMR of (a) epoxidized natural rubber and (b) degraded ENR after reaction with 0.075 mphr H_5IO_6.....94

Figure 4.36: The ratio of the integration area of the signal at 5.11ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after degradation with different amounts of H_5IO_6. 95

Figure 4.37: (A) Changes in absorbance of the double bond region (=C-H wagging) after 10 h reaction with various amounts of $KMnO_4$: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr $KMnO_4$. (B) Ratio of A_{835}/A_{2962} of ENR degraded at different concentrations of $KMnO_4$.....97

Figure 4.38: (A) Changes in absorbance of the carboxyl groupafter 10 h reaction with various amounts of $KMnO_4$: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr $KMnO_4$. (B) Ratio

of A_{1717}/A_{2962} to the C-H symmetrical stretching vibration of the degraded ENR with different amounts of $KMnO_4$. 97

Figure 4.39: ^{1}H-NMR of (a) epoxidized natural rubber and (b)degraded ENR after reaction with 0.075 mphr $KMnO_4$..... 98

Figure 4.40: The ratio of the integration area of the signal at 5.11 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after degradation with different concentrations of potassium permanganate. 99

Figure 4.41: (A) Changes in absorbance of the double bond region(=C-H wagging) after different UV irradiation times: a, after 3 h; b, after 5 h; c, after 8 h; d, after 18 h; and e, degraded NR under the same condition after 10 h irradiation . (B) Ratio of A_{835}/A_{2962} in the degraded ENR during UV irradiation. 100

Figure 4.42: (A) Changes in absorbance of the carbonyl group after different UV irradiation times: a, after 3 h; b, after 5 h; c, after 10 h; d, after 18 h; and e, degraded NR under the same condition after 10 h irradiation. (B) Ratio of A_{1717}/A_{2962} in the degraded ENR during UV irradiation. 101

Figure 4.43: (a) ^{1}H-NMR of epoxidized natural rubber; (b) degraded ENR by UV irradiation. The peaks at 1.83 ppm and 3.72 ppm could be related to hydrofuranic structure. 102

Figure 4.44: The ratio of the integration area of the signal at 5.11 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after different UV irradiation times. 102

Figure 4.45: (A) Changes in absorbance of the carbonyl group. A comparison of three degradation methods: a, product of degradation by 0.026 mphr H_5IO_6; b, product of degradation by 0.044 mphr $KMnO_4$; c, degraded ENR 25 after 5 h UV irradiation. (B) Ratio of A_{1717}/A_{2962} of different degradation methods..... 104

Figure 4.46: The decrease of log M_n during reaction time: a, degraded ENR by 0.075 mphr of H_5IO_6; b, degraded ENR by 0.075 mphr of $KMnO_4$; and c, degraded ENR by UV radiation. 104

Figure 4.47: Proposed reaction pathway of degradation of ENR by higher amount of H_5IO_6. 108

Figure 4.48: A suggested mechanism for cyclization of ENR in present of H_5IO_6. 109

Figure 4.49: Presumed mechanism of degradation reaction of ENR in the presence of $KMnO_4$ 109

Figure 4.50: FT-IR spectra of (A) LENR6 and (B) LENR-*graft*-MMA (GLENR2). . 114

Figure 4.51: ^{1} H-NMR spectrum of the LENR-g-PMMA (GLENR2). 116

Figure 4.52: DSC curves of (A) ENR, (B) LENR6 and (C) LENR-*graft*-PMMA (GLENR2). 116

Figure 4.53: FTIR spectra of (A) GLENR, (B) GLCO1, (C) GLCO2, (D) GLCO3. .. 120

LIST OF TABLES

Table 2.1: Dissociation energies of bonds in NR. 25

Table 2.2: Diffusion Data for Water through Organic Films. 39

Table 2.3: Typical examples of resin types. 40

Table 2.4: The estimated world market usage for different types of curing agents. 42

Table 3.1: Amount of each variable reactant added to the reaction mixtures for degradation with $KMnO_4$. 49

Table 3.2: Amount of each variable reactant added to the reaction mixtures for degradation with H_5IO_6. 49

Table 3.3: Amount of each variable reactant added to the reaction mixtures. 50

Table 3.4: Properties of grafted LENR (GLENR2). 55

Table 3.5: Properties of curing agents. 55

Table 3.6: Classification of adhesion test results. 58

Table 4.1: Absorbance ratio in the double bond and carbonyl region to C-H stretching of methyl group after mastication. 62

Table 4.2: Results of average molecular weight and polydispersity index after milling. 64

Table 4.3: Ratio of absorption of different functional groups to C-H stretching of methyl group after reaction with $K_2S_2O_8$. 66

Table 4.4: Ratio of absorption of different carbonyl and hydroxyl groups to C-H stretching of methyl group after reaction with $K_2S_2O_8$. 68

Table 4.5: Results of average molecular weight and polydispersity index after reaction with $K_2S_2O_8$ 68

Table 4.6: Results of average molecular weight and polydispersity indexafter UV irradiation. 78

Table 4.7: Results of epoxy equivalent weight of LENR obtained by different degradation methods. 80

Table 4.8: Results of average molecular weight and polydispersity during degradation with H_5IO_6 after 10 h of reaction. 95

Table 4.9: Results of average molecular weight during degradation with $KMnO_4$ after 10 h of reaction..... 99

Table 4.10: Results of average molecular weight and polydispersity after UV irradiation. 102

Table 4.11: Results of epoxy equivalent weight degraded ENR25 obtained by different degradation methods. 105

Table 4.12: Results of epoxy equivalent weight of LENR obtained from reaction at 10 h with H_5IO_6 at different concentrations. 106

Table 4.13: Effect of initiator concentration on graft copolymerization..... 113

Table 4.14: Chemical and physical properties of the coating materials..... 117

ABBREVIATIONS

^{1}H-NMR	Proton nuclear magnetic resonance
AIBN	Azobisisobutyronitrile
ASTM	American Society for Testing and Materials
DGBA	Diglycidyl ether of Bisphenol A
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DPNR	Deproteinized natural rubber
DRC	Dry rubber content
DSC	Differential Scanning Calorimetry
EA	Elemental analysis
ENR	Epoxidized natural rubber
ENR25	Epoxidized natural rubber with 25% mol of epoxidation
ENR50	Epoxidized natural rubber with 50% mol of epoxidation
EPI	Epoxidized polyisoprene
EPM	Ethylene-propylene rubber
FTIR	Fourier Transform Infrared
GLENR	LENR-*graft*-PMMA
GPC	Gel-Permeation Chromatography
HTNR	Hydroxyl-telechelic natural rubber
KHP	Potassium hydrogen phthalate
KPS	Potassium persulfate
LENR	Liquid epoxidized natural rubber
LNR	Liquid natural rubber
MEK	2-Butanone
MMA	Methyl methacrylate
M_n	Number average molecular weight
mol	Mole
mphr	Mol per hundred grams of rubber
M_w	Weight average molecular weight
MWD	Molecular weight distribution
NR	Natural rubber
p-TSH	para-toluene sulphonyl hydrazide
phr	Parts per hundred resin
PI	Polyisoprene
PMMA	Poly(methyl methacrylate)
PVC	Poly(vinyl chloride)
RRIM	Rubber Research Institute Malaysia
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
SMR	Standard Malaysian Rubber
T_g	Glass transition temperature
TGA	Thermogravimetry analysis
THF	Tetrahydrofuran
UV	Ultra violet
Vic	Vicinal

CHAPTER 1: INTRODUCTION

1.1 Research background

The natural rubber (NR) is a biopolymer isolated from the latex of Hevea brasiliensis tree which grows in tropical climate. The latex has a solid rubber content of about 30 w/w%. The rubber contains more than 95% cis -1, 4-polyisoprene and 5% non-rubbers (Mooibroek & Cornish, 2000). The natural rubber (NR) is a biopolymer isolated from the latex of Hevea brasiliensis tree which grows in tropical climate. The latex has a solid rubber content of about 30 w/w%. The estimated amount of energy needed to harvest and process of NR was 16 GJ/tonne compared to 130 GJ/tonne for synthetic SBR and 174 GJ/tonne for butyl rubber (Jones, 1994). Thus, with regards to energy demand, NR has greater advantage over synthetic rubbers.NR has been a strategic raw material that could not be replaced in some products, because of its outstanding technical characteristics, such as high resilience, excellent flexibility, resistance against splitting and impact resistance as well as excellent tensile strength and elongation properties (Lindley, 1981; Wang et al., 2000). These superior physical properties have made NR to be the only rubber usable for aircraft tires, 60% of heavy duty tires and more than 40% of car tires consist of NR. It is well known that manufacturing and usage of petroleum-based polymer and plastic is a source of environmental pollution. In contrast NR is an inherently environmental friendly. Due to depletion of petroleum and environmental concerns, various efforts have been devoted to produce new polymeric materials by chemical modifications of sustainable resources. The double bond in the repeating units of NR allows a number of chemical modifications such as vulcanization (Saville & Watson, 1967), epoxidation (Baker et al., 1985), cyclization (Riyajan, 2009;

Sakdapipanich et al., 2002), chlorination (Zhong et al., 1999), degradation (Sadaka et al., 2012) and grafting (Nakason et al., 2004a). NR also has some limitations. NR cannot be used in some industries such as coating and adhesives because of its processability due to its extremely high molecular weights and low solubility in organic solvents (La Mantia et al., 2017). Liquid natural rubber (LNR) is prepared by degradation of NR. The number average molecular weight (M_n) of LNR is less than 50000 (Nor & Ebdon, 1998) . Preparation of LNR has been an interesting subject for decades, because of its strong adhesive power and possibility for further chemical modifications. Several techniques have been employed to produce LNR. A phenylhydrazine/oxygen system was developed by Pautrat et al. (1980) to promote efficient oxidative degradation of NR. By varying the amount of phenylhydrazine in this system, the desired molecular weight of LNR can be achieved. However, this method suffered the shortcomings of removal of impurities and the dark brown colour of the product (Pautrat, 1980). To prepare light colour LNR, potassium persulfate is used for chain cleavage of polyisoprene (PI) but competitive reactions between chain cleavage and recombination of unstable terminal carbonyl groups have decreased the efficiency of degradation and difficulty in controlling the desired molecular weight of LNR (Tangpakdee et al., 1998) . The study of degradation by using periodic acid was carried out by Reyx et al. (1997). The ^{1}H NMR spectrum of the obtained product revealed the presence of cyclic structures as well as aldehyde and ketone moieties (Reyx & Campistron, 1997). Solar energy in presence of transition metal complexes was used by Tillekeratne et al. (Tillekeratne, 1977). Characterization of LNR showed that hydroperoxide, carboxyl, ester and aldehyde functional groups were present (Nor & Ebdon, 1998). Degradation of NR has been also carried out by thermal-oxidation (Li et al., 1998), ozonolysis (Perera et al., 1988), and mastication (Harmon & Jacobs, 1966) .

Each of these methods degrades NR through different mechanisms and create different amounts and types of functional groups.

One of the most important intermediate in organic synthesis is oxirane group. It has the ability to react with many other chemical groups such as amino, hydroxyl and carboxylic acid (Tanaka & Kakiuchi, 1963). Epoxidized natural rubber (ENR) is the product of partially epoxidation of double bonds of NR by a peroxy acid (Perera & Bradbury, 1992). Converting of NR to ENR improves several properties such as better oil resistance, lower gas permeability, better wet grip, higher damping characteristic (Gelling, 1991), glass transition temperature (T_g), and polarity (Kargarzadeh et al., 2015a). ENR has both unsaturation and oxirane groups that could be utilized for further chemical modifications (Baker et al., 1985).. During epoxidation, molecular weight remains unchanged, therefore ENR faces the same limitations in process ability and low solubility in organic solvents. Grafting is another valuable method for improving of properties of NR. Grafting of polar monomer onto NR improves thermal, weathering and oil resistance of the rubber (Moolsin & Robishaw, 2011). Furthermore, the low modulus and hardness of NR could be improved by incorporation of a hard segment such as polymethyl methacrylate onto NR. This incorporation could be done by grafting or blending. Grafted natural rubber by polar monomers has also better wettability and biocompatibility (Dafader et al., 2006). NR is mostly grafted with methyl acrylate, acrylonitrile and styrene. The degree of grafting is in the range of 60-80%. A graft copolymer "*Hevea plus MG*" based on methyl methacrylate natural rubber has been marketed in the middle of 20 centuries. "*Hevea plus MG*" has excellent properties such as electrical resistance, abrasion, hardness and modulus. Graft polymerization of NR with methyl methacrylate has been reported widely by different authors. Cooper et al. (1959) grafted methyl methacrylate onto natural rubber using ultra violet and γ ray as initiator. The results showed that the rate of copolymerization was first order with

respect to monomer concentration. It was concluded that by photo initiated graft polymerization the effect of temperature was very small. Several photo sensitizers were tested. The lowest efficiency belonged to azobisissobutyronitrile and the best yield was observed by 1-chloroanthraquinone. The grafting efficiency was dependent on reaction time, reaction temperature, initiator and monomer concentration (Cooper et al., 1959) .

1.2 Problem statement

ENR contains very useful technical characteristics as mentioned before. The good adhesion property of ENR and presence of oxirane group in the chemical structure could find its application in coating. However, ENR suffers the shortcomings of poor solubility in organic solvent, low T_g and incompatibility with most of the conventional curing agents used for ring opening and crosslinking of epoxy resins. Furthermore, uncured ENR suffers from softening at high temperatures and increased rigidity at low temperatures (Aprem et al., 2005). To improve the processability and solubility ENR could be degraded to decrease its molecular weight to less than 12000. On the other side graft copolymerization of methyl methacrylate onto ENR could increase the T_g and weathering resistance due to reduction in the amount of unsaturation some extent. Furthermore, mixing of ENR with poly aliphatic amine as curing agent results in separation of the rubber phase (Moolsin & Robishaw, 2011). Graft polymerization of methyl methacrylate monomer could improve the phase separation and make it more compatible with curing agents. Among the different degradation methods reported, there is a lack of study which compare these methods under similar conditions. In first part of our work we compare three different methods which degrade ENR25 through radical mechanism. In the second part the product of chemical oxidation of ENR is studied and compared. In the last part of our work MMA is grafted onto LENR obtained, to improve

its overall properties. The obtained grafted resin was cured with three different amine and amine adducts to find out which curing agent gives the best performance.

1.3 Objectives

The current study is carried out with the following objectives:

a) To investigate degradation of ENR through radical mechanism using three different methods. The three selected degradation methods are (i) mechanical milling, (ii) radical oxidative degradations by potassium peroxodisulfate, and (iii) photo-oxidation initiated by ultra violet (UV) irradiation.

b) To investigate degradation of ENR through chemical oxidation using H_5IO_6 and $KMnO_4$.

c) To graft methyl methacrylate to LENR obtained from UV degradation, and using the grafted LENR as a resin for coating by curing it with different curing agents.

CHAPTER 2: LITERATURE REVIEW

2.1 Natural rubber

NR is currently ranked as the fourth most important natural resource after air water and petroleum (Cornish, 2001) .The history of application of NR dates back to 1300 B.C., when Olmec civilization in South America used rubber to make rubbery goods and balls. In 1770, Jose Priestly noticed that rubber could erase pencil marks. Macintosh discovered that rubber could be used for water resistance finishing. He applied a solution of rubber onto a cotton cloth, and it became water resistance. The first product of vulcanized rubber was developed by Goodyear in 1893, the discovery which made NR one of the most important and strategically products (Ikeda, 2014). NR is currently used in different products such as tires, health equipment, adhesives, rubber springs, vibration mounts, etc. Nearly 2500 plant species produce latex, but the *Hevea brasiliensis* is the only commercial source of NR. The uncertainty in oil price and demands for oil replacement are disadvantages for production of petroleum based polymers and rubbers. It has led to an increase in the demand for NR which comes from a sustainable resource (Warren-Thomas et al., 2015). In 1876 *Hevea brasiliensis* was successfully transplanted from the Amazon to the Malaya Peninsula and Ceylon in South East Asia. The global NR production in 2013 was 11.15 million tonnes, which had an increase of 4.7% compared to the year before (Rasutis et al., 2015). About 90% of NR are produced in South-East Asia. NR consists predominantly of cis-1,4-polyisoprene. Isoprene is produced by different kind of trees. The emission of isoprene allows protects plants against heat stress. Polyisoprene is produced by adding activated isoprene molecule, isopentenyl diphosphate, to the growing chain. Cis-

prenyltransferases catalyses the polymerization reaction (Schmidt et al., 2010).The colloidal suspension gathered from Hevea brasiliensis is called NR. The tapping normally is done three times per week. The latex will be coagulated from suspension using formic acid. NR collected contains 30 -35% rubber. After centrifugation of the latex, the rubber content will increase to 60 %. To retard bacterial growth and increase the pH, ammonia is added to the latex. Treated NR contains 0.2-0.7% NH_3. The rubber content depends on soil properties, age of the tree and seasonal effect (Subramaniam, 1995). Young trees produce NR with lower content of molecular weight (M_n) because of incomplete biosynthesis of the rubber chain (Kovuttikulrangsie & Tanaka, 1999). Tangpakdee et al. (1996) reported that an increase in the age of the tree can cause a rise in M_n of NR. In gel permeation chromatography (GPC) the molecular weight distribution (MWD) could be unimodal, if only one peak appears but by appearance of several peaks the MWD is multi modal. The trees younger than two years shows a unimodal MWD (Tangpakdee et al., 1996). As the tree ages, a skewed uni or bi modal MWD could be observed, in which the high weight average molecular weight (M_w) peak is bigger than the low M_w peak (Kovuttikulrangsie & Sakdapipanich, 2004). The M_w is in the range of 104-107 g/mol and polydispersity ranging from 2.5 to 10. Size distribution of rubber particles in the latex phase is in between 0.05 micron to 0.3 micron (Sakdapipanich et al., 2002). NR could not crystallize under ordinary condition and it exists as amorphous rubbery material. In opposition to NR, Gutta-percha is formed from trans- 1, 4-polyisoprene, and has more regular conformation. It is able to crystallize under normal conditions and hence exist as rigid hard material (Nor & Ebdon, 1998). There are other impurities inside NR such as: 1) neutral lipids, 2.4%, 2) proteins, 2.2%, 3) glycolipids and phospholipids 1%, 4) carbohydrate, 0.4%, 5) ash, 0.2%. Several amino acids inside NR can cause allergic response during usage of products based on NR; therefore, sometimes deproteinized NR will be preferred to use.

However, there are many applications that NR could not be replaced by synthetic rubber such as jet and air craft carriers where NR offers better mechanical performance. There were many attempts to synthesize NR .The best result was reported by Halasa et al. using Ziegler-Natta and metallocene catalyst which yielded the highest cis isoprene content of about 98.5% with average number of molecular weight of 200000 g/mol (Halasa et al., 2007). However, so far none of the synthetic polyisoprene have been able to match the mechanical performance of NR.

2.2 Modification of Natural rubber

NR is used to make more than 40000 different products. This wide range of application is due to the possibility of modification of NR to obtain the desired properties. There are two main kinds of modification such as: Physical modification and chemical modification.

2.2.1 Physical modification

Physical modification could be done through blending of NR with other polymers or materials such as carbon black. Blending is considered as the simplest and most adaptable techniques for developing new materials. It is essential to have the ability to anticipate and comprehend the physical, mechanical properties and morphology of the blended polymer. Polymer blending could result in a homogeneous phase or separated phases or a mixture of both. The amount of homogeneity is dependent on several factors such as processing temperature, solvent properties and additives that are employed (Rameshwaram et al., 2005). The majority of polymer blends are observed to be immiscible. The process which alters the interfacial properties

of immiscible blends is called compatibilization. Compatibilization is based on the concept of reducing interfacial tension coefficient, which can lead to stabilization of desired blend morphology. A blend compatibilizer could be a macromolecule having interfacial activities in the heterogeneous polymer blends (Koning et al., 1998). There are different methods of polymer blending such as: 1) roll milling, 2) melt blending, 3) solvent blending, 4) latex blending. The properties of a blended polymer are dependent on the nature of its constituents, phases and phase continuity. T_g, modulus and morphology could explain the properties of a blended polymer (Favis, 2000) . NR is a non-polar polymer and suffers from poor heat resistance, ozone resistance and low oil and organic solvent resistance. Blending of NR with polar polymers could improve specific properties of NR. The polar polymers with groups such as acrylonitrile, fluorine, epoxy, carbonyl and chlorine have great resistance to swelling to oil and organic solvent. For example blending of NR with chloroprene rubber increases the resistance against heat and ozone (Thomas et al., 2013). The oil extended NR is the product of blending NR with oil which has application in tire industry to enhance skid resistance of tire on wet roads (Corish, 1967). Blending of polypropylene with NR with definite composition has properties of vulcanized rubber such a resilience and flexibility but can soften with heat, like thermoplastic polymers (Ismail, 2002) . Nitrile polymer (copolymer of acrylonitrile and butadiene) has excellent oil resistant property due to presence of acrylonitrile. The higher the proportion of acrylonitrile the greater is the oil resistance. Blending of NR and nitrile rubber enhances the characteristic properties of both polymers. The vulcanized blend (NR and nitrile rubber) has good strength resistance similar to NR and great resistance to swelling to oil similar to nitrile rubber (Jones & Tinker, 1997). Blending of ethylene –propylene (EPM) copolymer with NR has a great economical advantage due to the cheap price of NR. Electrical resistance and great ozone resistance are prominent properties of blended NR with

EPM. This material is mostly used as electrical protection sheathing (Jones & Tinker, 1997). The second kind of physical modification is deproteinizing of NR. Deproteinized NR has better mechanical properties due to increased hydrocarbon content and decreased nitrogen and ash content. Removal of protein reduces the moisture sensitivity and so it finds more usage in electrical and engineering industry. Besides deproteinized natural rubber has less allergic effect compared with NR (Manroshan et al., 2009).

2.2.2 Chemical modification

There are three kinds of chemical modification such as: 1) Modification by bond rearrangement such as cyclisation, cis-trans isomerization, carbon- carbon crosslinking and depolymerisation (Lee et al., 1963), 2) Grafting a new polymer onto NR backbone and 3) Modification by introducing of new chemical groups like chlorine and epoxy such as epoxidized natural rubber.

2.2.2.1 Cyclization

Cyclization of NR is done by treating of NR with acid catalyst at elevated temperature (not more than 140ºC). Intermolecular cyclization of neighboring unit could occur by various acid and Friedel-Crafts catalyst. Lewis acids such as $TiCl_4$, $SnCl_4$, $FeCl_3$ and BF_3 have been used for cyclization (Mirzataheri, 2000) . During cyclization, mono cyclic structure and poly cyclic structure could be formed. The resulting product is very brittle but still shows some elastic behavior (Hashim et al., 2002). Property and structure of cyclized rubber is related on the reaction condition and cyclization agent. The product of cyclization of NR is resistant to alkalis and acids; therefore, it is used in anti-corrosion and marine coatings. Cyclized rubber also finds application in adhesive

industry (Mirzataheri, 2000). Cyclized NR has greater tensile strength, abrasion resistance and hardness compared to NR. During cyclization of NR a drop in viscosity is observed which is caused by the decrease in the effective volume of the polyisoprene molecule and also degradation of long chain molecules of NR. During cyclization the empirical formula of NR does not change but a partial loss of unsaturation is observed (Lee et al., 1963). Several methods have been used to determine the degree of cyclization of rubber such as titration with bromine, Wijs method, hydro chlorination, iodometric titration and titration by thiosulfate after reaction with per benzoic acid. Lee et al. (1963) reported that using per benzoic acid is the most effective method for determination of unsaturation.

2.2.2.2 Cis-trans isomerization

Several unsaturated and conjugated polyolefins could undergo cis-trans isomerization under UV exposure and in presence of sulfur and bromide compounds. However, this method is not effective to interconvert the isomerization of NR. Cis-trans isomerization of NR was achieved by treatment with SO_2 at 140ºC after 24 h (Cunneen, 1960). The product contains 43% of cis double bond and 57% of trans double bond. This ratio is the equilibrium composition for isoprene (Cunneen et al., 1959).

2.2.2.3 Vulcanization

The most important process in rubber industry is vulcanization (crosslinking). Initially NR was utilized uncured and suffered from softening at high temperature and increased rigidity at low temperatures (Aprem et al., 2005). Charles Goodyear in 1890 discovered a process called vulcanization. This process could enhance strength and the

elastic property of rubber due to formation of three-dimensional network by cross-linking between rubber macromolecules. The tendency of crystallinity noticeably decreases by vulcanization of rubber and the solvent resistant enhances significantly. Poly and mono sulfidic crosslinks are created between the rubber chains and accordingly reduce drastically the movement of the chains (Morrell & Blow, 1982). Different chemicals have been used to vulcanize rubber such as sulfur, quinone, metal oxide and peroxide (Mark et al., 2013). Vulcanization has been done by different energy sources such as heat, irradiation, microwave energy and ultrasound. The cross link formation and vulcanization rate could be determined by a rheometer or oscillating disk (Morrell & Blow, 1982). There are three stage in vulcanization process, namely: induction, curing and over cure. The period of time before crosslinking begins is called induction or scorch. Curing is the time frame within the cross-linking reaction begins. In over cure stage crosslinking destruction and cross linking inter change appears. By plotting torque against time in over cure stage torque remains unchanged or decrease slightly. There is an optimal value in crosslink density in that the tensile strength is maximum. By further increase in crosslink density as occurs in over cure stage, tensile strength decreases (López-Manchado et al., 2003).The vulcanization reaction has been improved by invention of organic accelerators, retarders and activators. The accelerators are usually derivatives of alkyd dithiocarbamic acid and mercaptobenzothiazole. Zinc oxide, nitrogenous base and fatty acid are used as activators in vulcanization process. The role of activators is to make accelerators perform more effectively. The ratio of sulfur to accelerator has a great influence on the cross-linking reaction. A low ratio of sulfur to accelerator causes high proportion of mono sulfidic crosslinks, which has better heat resistance. A high ratio produces longer cross-links with higher strength (Aprem et al., 2005). Activated accelerator reacts with cyclic sulfur molecule and creates active sulfur complex. The complex is unstable and self-destroyed with

producing radicals which attack isoprene in the rubber chain and create sulfur-rubber intermediate. The sulfur rubber intermediate could attack another rubber chain to make polysulfidic links between the rubber molecules. Dynamic vulcanization is the process of vulcanizing a polymer in its molten state, while it is mixed with other polymers which are inert to vulcanization reaction. Dynamic vulcanization is used widely to produce thermoplastic polymers (Aprem et al., 2005).

2.2.2.4 Chlorination

Chlorination of NR includes substitution of hydrogen atoms by chlorine or addition of chlorine to the double bonds (Figure 2.1). Rubber solution in carbon tetrachloride reacts with gaseous chlorine or with dissolved chlorine in CCl_4. In this reaction hydrogen chloride is produced immediately. The initial stage of the reaction is substitution of hydrogen atom in the secondary allylic position with chlorine (Brock et al., 2000). The properties of chlorinated rubber are closely related to the chlorine content. In exposure of light or heat chlorine could split off as HCl; therefore, in the rubber with lower chlorine content a deterioration of the mechanical properties is observable over the time. Accordingly if the chlorine content is high the rubber is more stable (Van Amerongen et al., 1950). The chlorinated product with 65% chlorine content is very stable and is used as anticorrosive coating. Chlorinated rubber shows enhanced resistance to chemicals, weather and water as well as lower water permeability. As alternative to vinyl chloride polymer, chlorinated rubber is used for weather proofing and corrosion protective marine coatings (Zhong et al., 1999). A drawback of application of chlorinated rubber in coatings is the possibility of reaction with ZnO pigment. The reaction can cause pigment and resin to degrade and release

HCl. At temperature higher than 60º the same decomposition is observed so the usage of chlorinated rubber is not appropriate at elevated temperature (Brock et al., 2000).

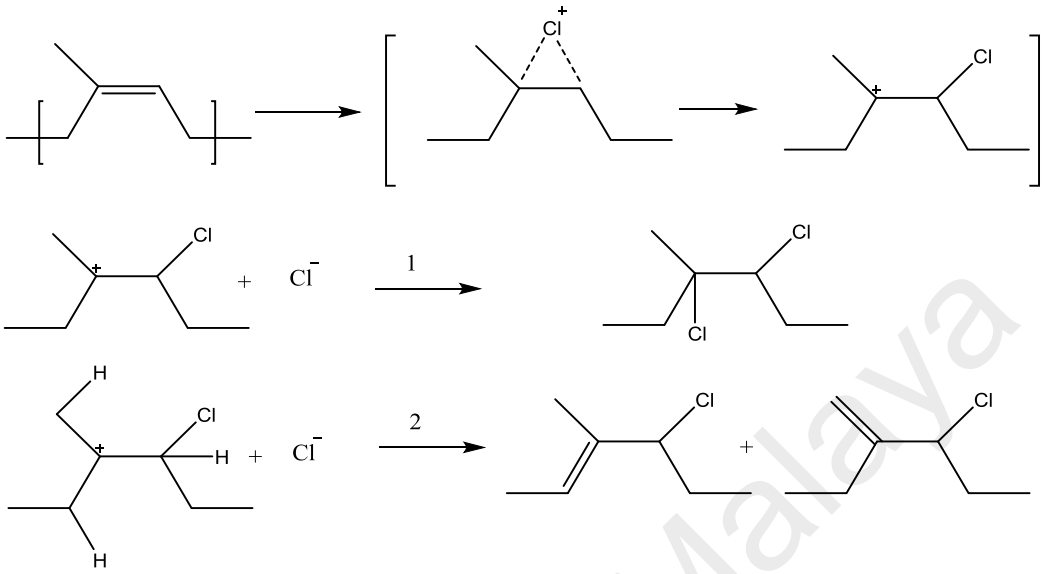
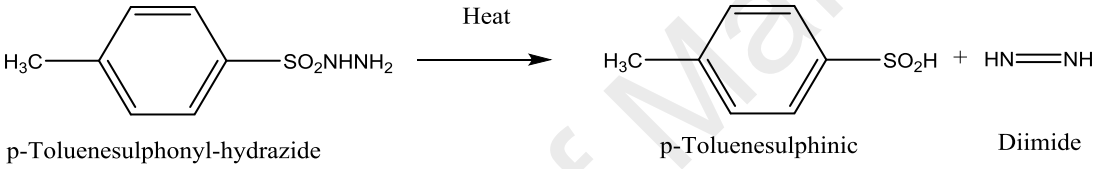


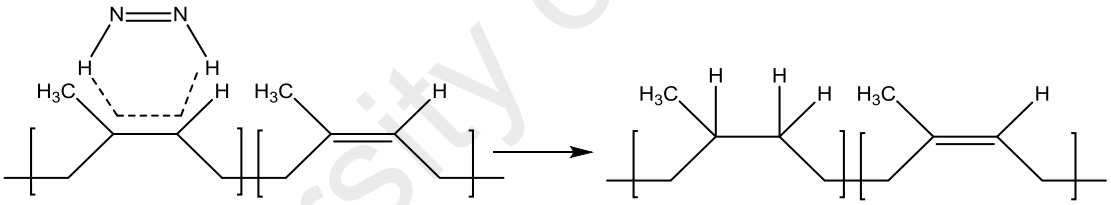
Figure 2.1: Chlorination of NR: (1 Addition reaction. (2 Substitution reaction.

2.2.2.5 Hydrogenation

Polymers with olefinic units have a low resistance to heat and hydrogenation of NR can enhance resistance to heat and oxidative degradation through saturation of isoprene. Furthermore, hydrogenated isoprene shows lower gas permeability and better resistance to oil in comparison with NR. Thermal properties of hydrogenated NR increase along with the rise in degree of hydrogenation without noticeable change in T_g. These new properties increase the application of hydrogenated NR in various industries including military, automotive and aerospace (Samran et al., 2005). Catalytic hydrogenation of NR could be carried out by heterogeneous or homogenous catalysts. Hydrogenation could be done by using hydrogen gases in the presence of metal catalysts such as Ni, Pd and Pt. Hydrogenation with a heterogeneous catalyst such as Pd has a yield of 8% hydrogenation mainly due to sticky nature of NR that can contaminate

the surface of catalyst (Phinyocheep, 2014) Complete hydrogenation of NR was reported by Singha et.al, using $RhCl(PPh_3)_3$ as catalyst. They reported that the degree of hydrogenation is related to concentration of catalyst and NR(Singha et al., 1997) . Diimide (N_2H_2) is also capable to release and transfer H_2 to unsaturated isoprene unit. Hydrogenation using diimide could be carried out under low pressure and utilizing simple apparatus. Oxidation of hydrazine or decomposition of arenesulphonylhydrazides by heat could produce diimide. Para-toluenesulphonylhydrazide (p-TSH) has been carried out for hydrogenation of NR (Samran et al., 2005). p-TSH decomposes at 135ºC and generates diimide and para-





toluenesulfonic acid (Figure 2.2). 1 mol of p-TSH could hydrogenize one mol of C=C bond. The drawback of this reaction is the presence of para-toluenesulfonic acid which causes cis-trans isomerization in the isoprene unit.

Figure 2.2: Hydrogenation of NR using p-TSH at 135 ºC.

2.3 Epoxidized natural rubber

Epoxidized natural rubber (ENR) as commercial product was produced in the 1980. NR could be easily epoxidized in solution by peroxy acids such as peracetic,

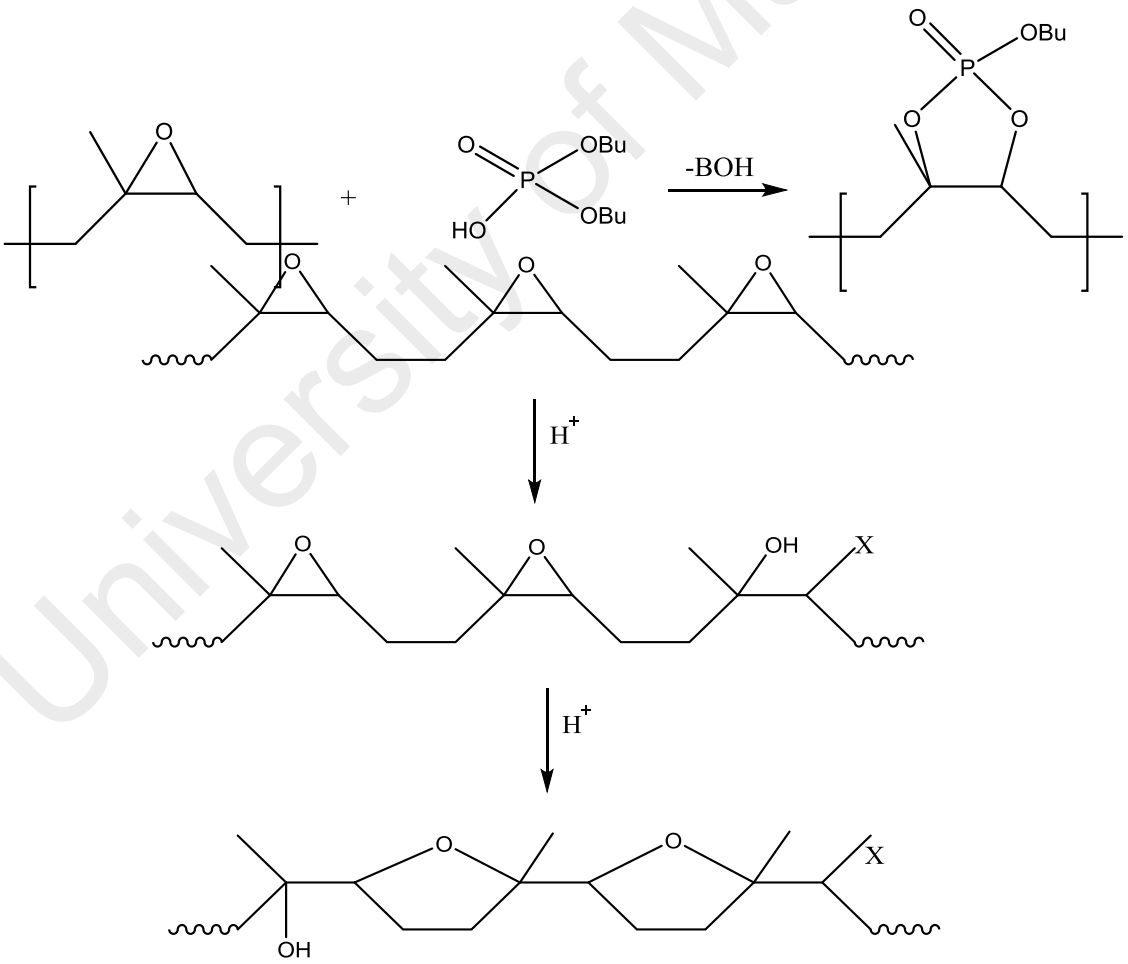
perbenzoic acid etc. Epoxidation could be done in latex form as well as in organic solutions (Azhar et al., 2017). In industrial epoxidation process, two main reagents are used: peroxyacetic acid or mixture of formic acid and hydrogen peroxide. Epoxidation reaction can go further to reach any desired epoxy content. Among various organic peroxyacids only m-chloroperbenzoic acid could react quantitatively with the double bond. The activation energy for epoxidation reaction is 56.2 kJ/mol. The yield of epoxidation is related to reaction time and concentration of NR and peroxyacid (Vernekar et al., 1992). During epoxidation several side reactions occur which introduce functional groups such as tetrahydrofuran, hydroxyl and ester groups into the NR chain (Burfield et al., 1984).There is a linear enhancement of T_g with increase in epoxy content. By 1 mol % increase in epoxy content, T_g increase around 1º C. ENR with 25 mol% epoxidation (ENR25) has a T_g of -47º C, while T_g of ENR with 50 mol% epoxidation (ENR50) is -22º C (Gelling, 1991). The increase of T_g is expected to enhance many properties of ENR such as better and stronger bond to metal, tensile strength, fatigue behaviour and wet grip. Wet grip is an important measurement of tire safety. The tires with better wet grip, exhibit shorter distance to halt on wet road when brake is applied (Hashim et al., 2002).NR is susceptible to crystallization at low temperatures. Crystallization of NR leads to significant changes in mechanical performance. A nonlinear increase in density and Young's modulus is observed with rise in degree of crystallization. Low temperature crystallization does not occur in ENR25 and ENR50 (Fuller et al., 2004). The characteristic peak of oxirane group in IR spectrum appears at 870 cm^{-1} and belongs to stretching vibrations of (cis C-O). Characterization peak of NR appears at 835cm^{-1} which is related to cis double bond (=C-H). In the NMR spectrum, the methine proton adjacent to oxirane group appears at 2.68 ppm while the methine proton attached to the double bond has a peak at 5.14 ppm. By dividing of integration area of these two methine protons epoxy content could be

measured. There are also other methods for calculation of epoxy content of ENR such as direct titration with hydrogen bromide acid, differential scanning calorimetry (DSC) technique and elemental analysis (EA). DSC results of ENR have shown that increase in epoxy content linearly affected the increase of T_g (Burfield et al., 1984). By increasing the epoxide content various properties of ENR are improved such as polarity, and air permeability. The increase in polarity of ENR can result in more resistance to oil and nonpolar solvent, while it deteriorates resistance to polar solvents. In the same manner, the tack of ENR towards nonpolar polymers decrease, but on the contrary the compatibility with polar polymer enhances obviously. Oil resistance of ENR 50 is comparable to acrylonitrile butadiene rubber and also its air permeability is similar to butyl rubber (Baker et al., 1985) . Because of the improved oil resistance ENR could be utilized for oil -contact engine parts such as seals tubes and hoses (Phinyocheep, 2014). Oxirane group could undergo both electrophilic and nucleophilic attacks. Therefore, in the epoxidation process due to presence of acid, ring opening could occur. In the ring opening of epoxide both steric and electronic factors are important. The final product of ring opening of epoxides by an acid is trans diols. Ring opening of adjacent epoxide

groups could yield in a five-membered cyclic ethers as shown in Figure 2.3 (Gelling, 1991).

Figure 2.3: Formation of five- membered cyclic ethers by ring opening of oxirane group.

The reactivity of ENR towards nucleophilic reagents allows a great number of chemical modifications. Addition of phosphorus containing reagents to improve inflammability of ENR is an example of these modifications. Incorporation of dibutyl phosphate to the chain of ENR to decrease the flammability of rubber was reported by



Derouet et al. (1994) (Figure 2.4).

Figure 2.4: Incorporation of dibutyl phosphate to ENR by ring opening of epoxide.

There has been a growing interest in blending of ENR and other thermoplastic polymers over the recent years. The free Gibbes energy of a compatible blend is negative. Due to high molecular weight of polymer the entropy of mixing is usually small. Intermolecular interactions of two polymers are responsible for the miscibility of blends. Blending of NR with PMMA without compatibilizer exhibit poor mechanical properties (Nakason et al., 2004b). Intermolecular interactions of two polymers are responsible for the miscibility of blends. By adding polar group to NR, the inter-chain interactions between two polymers increase and therefore the property of blends can be improved. The oxirane group in ENR could interact with polar atoms in other polymers. The SEM analysis of ENR 25 and PMMA blends revealed a partial blend miscibility. Nakason et al. (2004) reported that ENR with different epoxy content could be blended with PMMA. ENR 25 is partially miscible with PVC but ENR 50 is completely miscible with PVC (Nakason et al., 2004c). DSC analysis of the blend of ENR 50 and PVC exhibited a single T_g which confirms that a miscible blend is obtained (Gelling, 1991). ENR finds application in tire industry, sport shoe soling and flooring materials due to its low gas permeability and good wet grip. ENR is also used for construction of PVC conveyer belts because of its high adhesion to PVC and high strength and low rolling resistance (Nguyen et al., 2009).

2.4 Liquid natural rubber and liquid epoxidized natural rubber

Liquid natural rubber (LNR) is the product of degradation of NR and consists of isoprene unit and terminal functional group. LNR has M_n less than 50000. Liquid epoxidized natural rubber (LENR) could be obtained from degradation of ENR. The

degradation methods of NR and ENR are similar but ENR degrades through cleavage of oxirane group and double bonds. At room temperature LNR is a sticky liquid and can easily flow, therefore its mixing process with other materials does not consume as much energy required for mixing of NR. Due to presence of terminal functional groups, LNR could be chain extended through double bonds or reactive terminal groups. This can improve the mechanical properties of vulcanized rubber. There are a variety of functional groups that could be added to LNR such as bromine, hydroxyl, vinyl, amine, phenyl and carboxyl (Berry & Morrell, 1974). But the most attractive and useful terminal groups are carboxyl and hydroxyl. Due to excellent adhesion power and strong cross-linking reactivity of LNR and LENR they have been utilized for adhesives, compatibilizers, reactive plasticizers, viscosity modifier and sealants (Nair et al., 1997).

2.4.1 Synthesis

Preparation of LNR and LENR has been an attractive subject to the scientists. There are 5 different methods for production of LNR such as photo degradation, metathesis , redox, oxidation of double bond using chemical reagents and degradation at high temperature (Kargarzadeh et al., 2014). LNR obtained from each method of depolymerization has specific properties depending on the used method.

2.4.1.1 Redox method

Redox method was developed by French scientists (IRCA) in 1976. In this method, both oxidizing and reducing agent are used at same time. Oxidizing agent could be atmospheric oxygen, $FeCl_3$, and H_2O_2, while phenyl hydrazine and sulfonic acid was utilized as reducing agent. The degraded rubber obtained by redox method has a molecular weight between 3000 to 35000 g/mol and polydispersity ranging from 1.7 to 2. This method could be employed either in organic solvents such as toluene or directly in latex phase. Atmospheric O_2 as oxidizing agent and phenylhydrazine as reducing agent are more favored and were studied in details. Pautrat et al. found that the M_n of degraded rubber with this method is related to the amount of phenylhydrazine employed, ratio of air flow, temperature and reaction time (Pautrat, 1980). Phenyl radical generated due to presence of oxygen and heat, attacks the double bond and creates tertiary alkyl radical. In the presence of oxygen unstable hydroperoxy radicals are formed which cause chain cleavage of NR. Addition of phenyl radical on double bond causes the formation of methyl and phenyl terminated LNR. Reyx et al. suggested the mechanism shown in Figure 2.5 for degradation of NR using phenylhydrazine and oxygen (Reyx & Campistron, 1997).

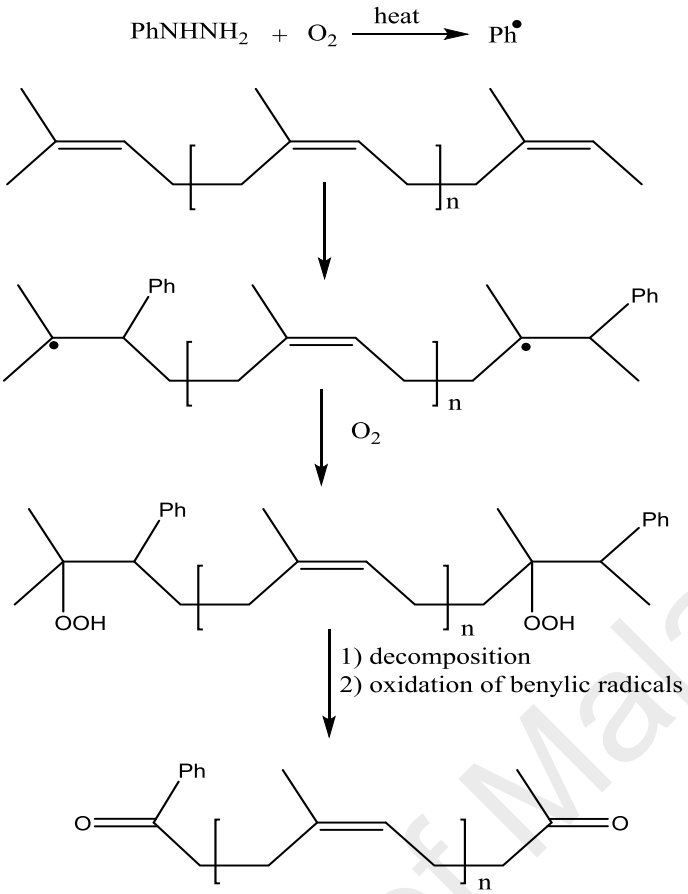


Figure 2.5: Synthesis of LNR using phenylhydrazine and oxygen as reducing and oxidizing agent .

2.4.1.2 Ozonolysis

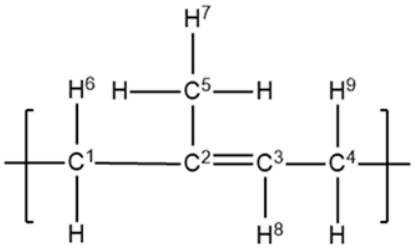
Ozonolysis of NR can be carried out in an organic solvent by blowing of ozone gas into the solution over a period of time. Thereafter the mixture is treated with a reducing or an oxidizing agent. The conventional oxidizing agents used in this method are hydrogen peroxide, potassium iodide in acetic acid and oxygen. Reducing agent could be sodium borohydride, triphenylphosphine, zinc in acetic acid and lithium aluminum hydride. Ozonolysis of NR and ENR begins by attack of ozone molecule to the carbon-carbon double bond to generate molozonide. Molozonide is unstable and cleaves to carbonyl oxide and carbonyl compound such as aldehyde or ketone. Carbonyl oxide is very reactive and attacks other carbonyl group to create primary and secondary ozonide which further cleaves by influence of heat or oxidizing agents to produce

aldehyde and alcohols. Ozonolysis of NR is a significant and convenient method for generation of unsaturated oligomers bearing active functional group such as hydroxyl, carboxyl, ketone and aldehyde. Ozonolysis of NR in chloroform at a flow rate of 1.73 g/h of O_3 was reported by Nor at el. The reaction was done at 0˚C and the M_n of NR decreased from 271000 to less than 900 within 20 minutes which is a significantly rapid method to prepare LNR. It has been found that degradation has occurred mostly in the first minute of reaction and the degraded NR showed a bimodal distribution of M_n. By proceeding of the reaction, M_n reached to 853 and the distribution of M_n became unimodal again. They had reported that very low molecular weight levulinaldehyde and levulinic acid were produced during ozonolysis. IR spectra of the ozonolysed rubber showed a decrease in intensity of peaks at 1450 cm^{-1} and 835 cm^{-1} related to the methylene group (-CH_2- deforming) and double bond (=C-H wagging) respectively. The peak at 1378 cm^{-1} assigned to methyl group (-CH_3 asymmetric deformation) did not change noticeably as the methyl group are not significantly affected by ozonolysis. Two new peaks with great intensity were observed at 1720 cm^{-1} and 3440 cm^{-1} which are related to carbonyl group and OH moiety. Another major change observed in the IR spectra was the appearance of characteristic peak of ozonide at 1084 cm^{-1}. Kodena et al. ozonolyzed high ammonia NR by bubbling ozone at a flow rate of 4g/h in the latex phase, with subsequent treatment with hydrogen peroxide. The degradation rate was related to the ozone concentration. Addition of hydrogen peroxide accelerated the degradation rate but a rise in hydrogen peroxide concentration did not show any further effect. Proceeding of reaction caused a decrease in initial pH from 8 to 6 which was due to formation of low molecular weight levulinic acid. They had demonstrated that degradation by ozone at pH below 8 do not go through the formation of ozonide but interaction between hydrogen peroxide and ozone creating hydroxyl and hydroperoxy radicals. Therefore, they suggested that the main reaction at acidic condition should be

radical oxidation (Kodama et al., 2003). As reported by Montaudo et al. the ozonolysis of NR in 0˚C in hexane did not lead to formation of ozonide but only telechelic oligomers bearing ketone and carboxylic acid. Degradation of unsaturated rubber by ozone is still a potential method to produce LNR bearing reactive oxygenated terminal groups (Montaudo et al., 1992).

2.4.1.3 Photochemical degradation

The energy of light with wave length of 300 nm to 600 nm is about 47 to 95 kcal. The dissociation energies of various bond of the polyisoprene are given in Table 2.1. From this table, it can be seen that energy of light is strong enough to lead to photochemical bond dissociation of NR resulting in production of free radicals. External initiator can be used to accelerate photo-degradation. External initiators such as dicumyl peroxide, 2,2- azobis-(isobutyronitrile), benzoyl peroxide, etc. can reduce considerably the induction period and generate free radicals. Impurities such as hydroperoxide and peroxide could act also as initiators. Even highly pure polymers contain these kind of impurities (Wiles & Carlsson, 1980). In some commercial resins, antioxidant and peroxide decomposer are used to reduce the amount of peroxide and hydroperoxide impurities.



Type of bond	Dissociation energy(kcal mole^{-1})
C^1-C^2	92.6
C^3-C^4	90
C^2-C^5	86.2
C^5-H^7	84
C^1-H^6	79.8
C^4-H^9	75.6
C^1-H^4	73

Table 2.1: Dissociation energies of bonds in NR.

The mechanism of photo degradation is assumed to involve radical attack either to the double bond (addition mechanism) or to hydrogen atom in the allylic position which lead to abstraction of the hydrogen atom. Presence of oxygen during radical attack leads to formation of peroxide, hydroperoxide, carbonyl function and alcohols (Bussière et al., 2005). The O_2 molecule is paramagnetic because of parallel spin of two unbonded electron. Therefore, oxygen molecule acts as biradical and could react rapidly with free radicals to form peroxy radicals. It is assumed that the molecular oxygen itself can also oxidize the weak C-H bond in α position of the double bond as is shown in Figure 2.6.

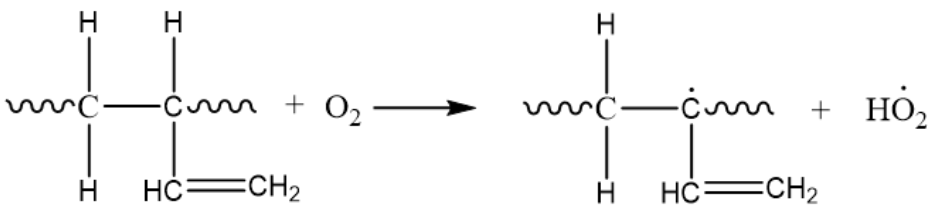
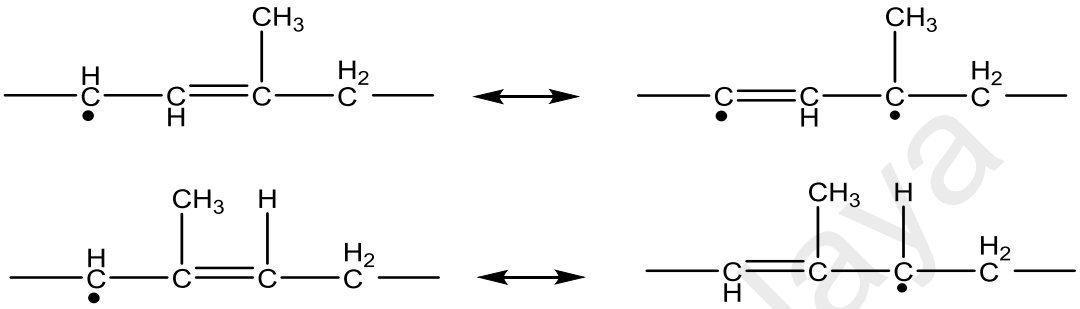


Figure 2.6: Scheme of abstraction of allylic hydrogen directly by oxygen molecule.

In photochemical degradation, there is always a competition between addition and abstraction mechanism(Adam et al., 1991). In the abstraction mechanism two different allyl radicals could be formed due to asymmetry of the isoprene unit (Figure



2.7).

Figure 2.7: Different allyl radicals could be generated by radical attack.

Allylic radicals in presence of oxygen molecule convert to proxy radicals. Peroxy radicals abstract hydrogen atoms and form hydroperoxide. Due to tertiary structure of hydroperoxide in polyisoprene a very high content of these species could be detected by chemical titration or by IR spectroscopy (Adam et al., 1991). At temperature below 35ºC tertiary hydroperoxide are stable and they are the major product of degradation. Hydroperoxide decomposes homolytically due to UV radiation, thermal energy and catalyst such as metal ions (Adam et al., 1991). Unbounded hydroperoxide has an absorption band at 3520 cm^{-1} but hydrogen bond with hydroxyl group change the band to about 3380 cm^{-1}. A new method for determination of hydroperoxide was reported by Mitchell et al. In this method, hydroperoxide reacts with SO_2. After treatment with SO_2 new bands appear at 1415 cm^{-1} 1195 cm^{-1} and 920 cm^{-1} and the band at 3520 cm^{-1} disappears (Mitchell Jr & Perkins, 1967). Hydroperoxide

could also decompose homolitically to yield biradical, which is transformed immediately to ketonic group (Figure 2.8).

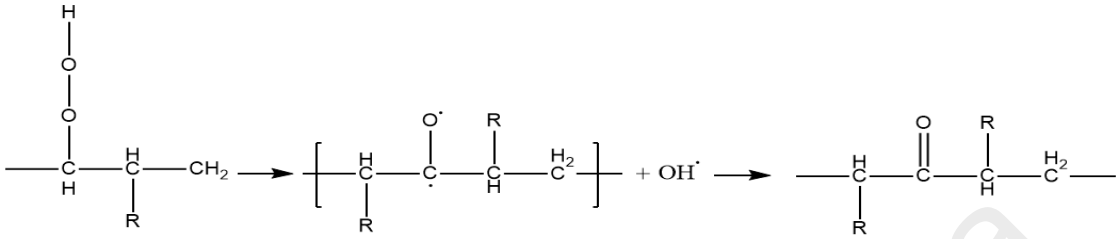


Figure 2.8: Homolytic decompositon of hydroperoxide to generate ketone.

Tertiary alkoxy radicals are formed by decomposition of hydroperoxide (Figure 2.9). The alkoxy radicals can be transformed either into alcohol, by abstraction of a hydrogen atom or they can split by the β scission process into ketone group (Adam et al., 1991).

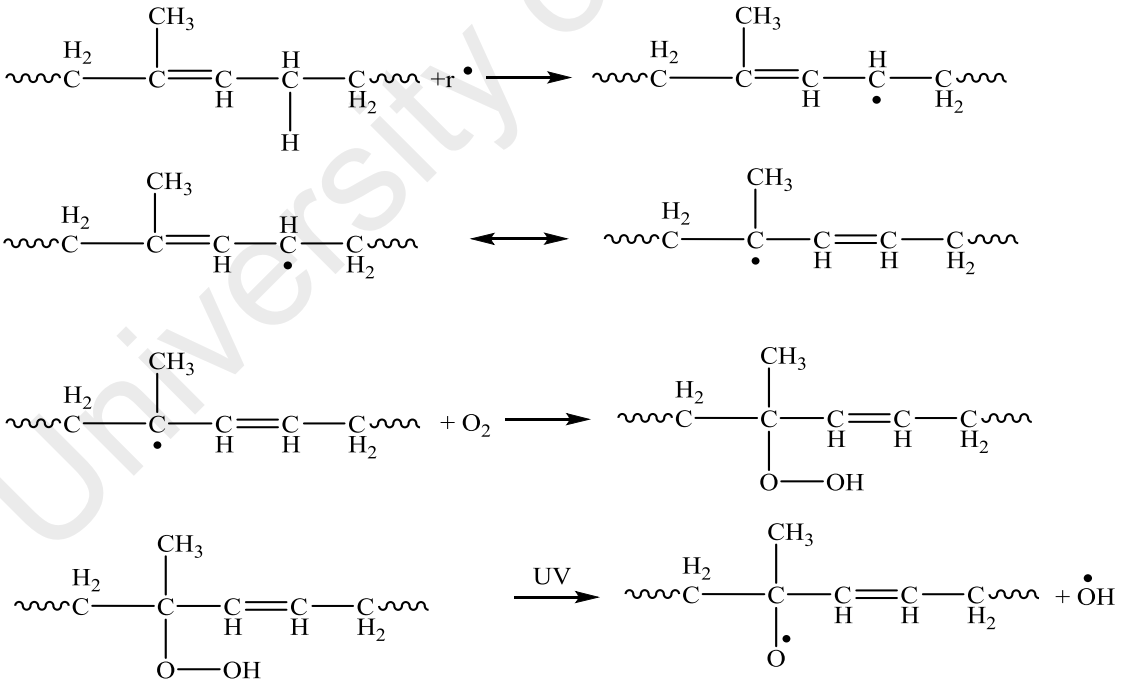


Figure 2.9: Formation of alkoxy peroxide through subtitution mechanism.

Addition of radicals directly to the double bond is probably the main degradation pathway (Adam et al., 1991). In this mechanism after formation tertiary alkyl radicals they react with oxygen to produce hydrogen peroxide (Figure 2.10).

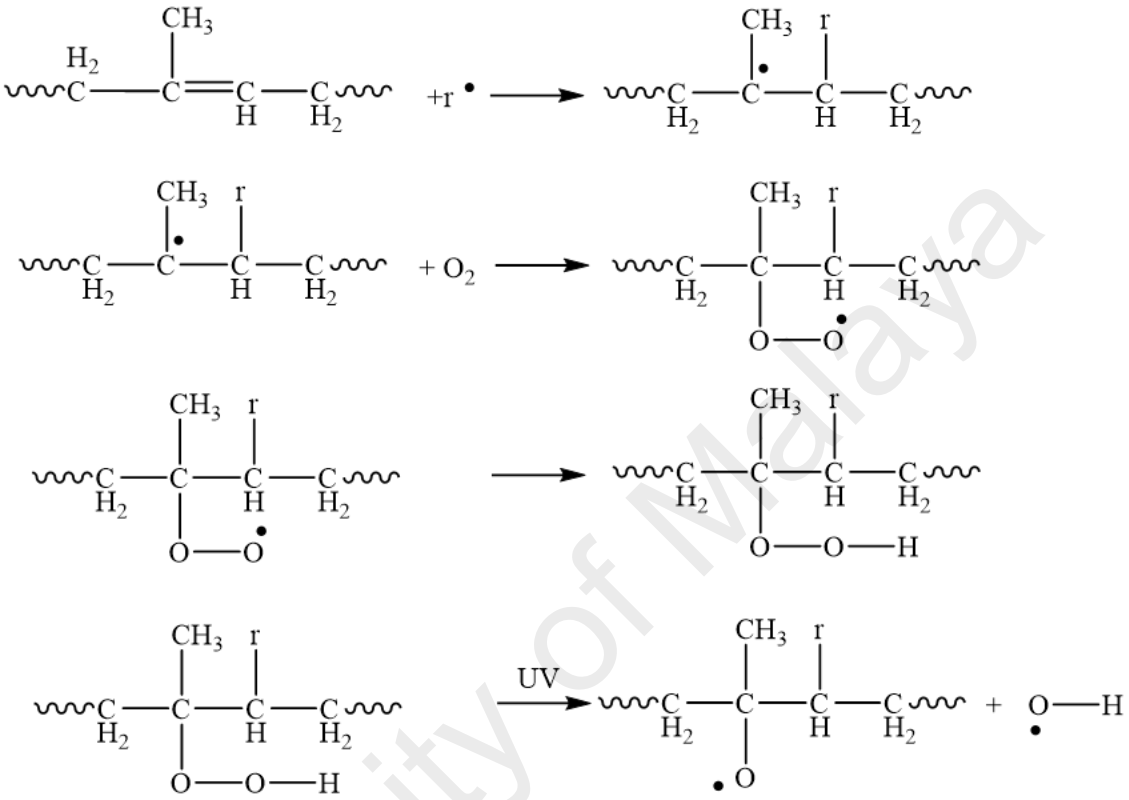


Figure 2.10: Formation of alkoxy peroxide by addition mechanism.

Ravindran et al. (1988) studied degradation of NR by UV and visible light in presence of hydrogen peroxide. It was reported that both sources of energies were able to degrade NR with similar efficiency. The main product was hydroxy-telechelic natural rubber (HTNR) and a lightly crosslinked LNR with carbonyl functional group in 10 % yield. The author also found that decrease in concentration of hydrogen peroxide and increase in exposure time have led to a significant reduction in the molecular weight of NR (Ravindran et al., 1988). Degradation of NR by sun-light and hydrogen peroxide was reported by Joseph et al. In this method HTNR obtained after 50 h exposure of

sunlight reached a M_n =7600. However no details of type of functional group was reported (Joseph, 1991). Kargarzadeh et al. (2015) degraded ENR and NR using visible light (fluorescent lamp, 40 watts) for 50 days exposure at 80° C. The M_n of NR decreased from $2x10^6$ to $2x10^5$ after degradation. IR spectra of degraded ENR and NR showed the presence of hydroperoxide and carbonyl on the backbone of the rubber. Furthermore a decrease in double bond density was observed (Kargarzadeh et al., 2015). Dos Santos et al. demonstrated that UV degradation of polyisoprene films depended the wavelength of UV irradiation; under 253 nm irradiation led to crosslinking of NR but at wavelength above 300nm chain scission prevailed. It was argued that there is competition between degradation and cross linkage mechanism in the photochemical degradation and the wave length of the irradiation determines the prevailed mechanism (Dos Santos et al., 2005).

2.4.1.4 Degradation using chemical reagents

Degradation of NR by chemical reagents has been widely investigated. Using chemical reagents for chain cleavage of rubber seem to offer the possibility to control the molecular weight of LNR and LENR, by varying the amount of reagent employed. Up until now different oxidants were used to degrade rubber to produce telechelic liquid rubber such as H_5IO_6, $K_2S_2O_8$, $Pb(OAc)_4$,$(NH_4)_2S_2O_8$, RuO_4 and Na_2WO_4. (Fainleib et al., 2013; Zhang et al., 2010). For depolymerization of ENR in latex phase, Phinyocheep et al. (2005) used periodic acid because of its good solubility in water. ENR was treated with periodic acid at 30ºC. The IR spectrum of product revealed that there were no changes in oxirane group during depolymerization but appearance of strong signals at 1721 cm^{-1} and 3460 cm^{-1} attributed to carboxyl group and hydroxyl function respectively (Phinyocheep et al., 2005). It was concluded that the chemical

structure of the degraded ENR is composed of isoprene unit, epoxidized structure, ketone and aldehyde end. The molecular weight deduction during chain cleavage was depended on reaction time whereby M_n of the degraded rubber obtained was around 500 g/mol after 21 h processing with H_5IO_6. During the different reaction times, no change in epoxy content was observed which implies that during depolymerization with periodic acid, oxirane group is not involved in the reaction mechanism; instead the reaction seems likely to have occurred via carbon double bond with an intermediate such as vic diols. The efficiency of degradation of NR under the same condition using periodic acid was definitely less than degradation of ENR as has been reported. It was concluded that faster reaction of ENR with periodic acid is due to higher polarity of ENR compared to NR. At prolonged reaction time, there was a small change in M_w but the intensity of carbonyl group continuously increased. Gillier-Ritoit el al. (2003) degraded synthesized epoxidized polyisoprene (EPI) with periodic acid. The reaction was done in different solvents such as THF and chloroform (Gillier- Ritoit et al., 2003). The yield of reaction with THF as solvent under the same condition was greater than chloroform. It was concluded that a correlation between epoxide content and degree of depolymerization exists. Moreover, the decrease in epoxy content in epoxidized polyisoprene is correlated to an increase in M_n, which means a decrease of reaction yields. Synthetic polyisoprene was also degraded with periodic acid. The results of EPI and PI showed that degradation of PI needed twice greater amount of periodic acid to achieve the same yield. Gillier-Ritoit el al. (2003) suggested a two-step mechanism for the reaction. In the first step periodic acid attacks the double bond and converts it to oxirane or vic diol. Oxirane or vic diol is cleaved by a second equivalent of H_5IO_6 (Figure 2.11). Gillier-Ritoit el al. (2003) experiments revealed that epoxy group is the main part of mechanism of degradation reaction. The cleavage of oxirane is very fast whereas the cleavage of double bond is a slow reaction (Gillier- Ritoit et al., 2003).

This observation is also another confirmation for two-step mechanism for degradation of double bond.

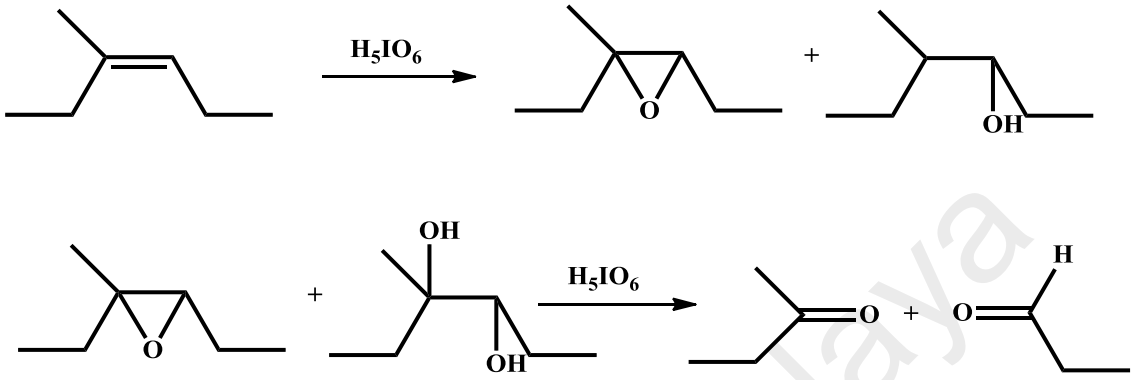


Figure 2.11: Two-step mechanism for cleavage of the doublebond by H_5IO_6.

Saetung et al. reported degradation of NR via a two-step procedure. In the first step NR was epoxidized by performic acid at 60 ºC and then it was degraded with H_5IO_6 at 30 ºC. After 8 h of reaction an epoxy content of 10% was achieved. After 6 h degradation with periodic acid the M_n dropped to 1980 g/mol. It was also observed that degradation of ENR containing higher epoxy content resulted in smaller M_n under the same condition. Saetung et al. reported that degradation of ENR in organic solvent had better yield in terms of M_n than in latex phase (Saetung et al., 2010) .Chaikumpollert et al. (2011) degraded NR with potassium persulfate (KPS) as a radical initiator at 30ºC. With increasing amount of potassium persulfate there were a greater decrease in Mooney viscosity of rubber. The IR spectrum revealed two new peaks at 1720 cm^{-1} and 1730 cm^{-1} that were identified as the formyl and carbonyl groups of aldehyde and ketone respectively. NMR showed a small signal at about 9.6 ppm which was assigned

to proton of formyl groups. The signal of methyl ketone which should appear at 2.1 ppm was not isolated due to overlapping with isoprene methyl protons. Chaikumpollert et al. (2011) concluded that during chain scission terminal formyl and carbonyl groups appeared. The suggested mechanism for oxidative degradation with KPS is chain scission at double bond of isoprene. The tensile strength of NR before degradation was 7.73 MPa which decreased to 1.6 MPa after degradation. NR and the degraded product were vulcanized in the same condition. The tensile strengths results revealed that the vulcanized rubber and the degraded one both had the same tensile strength of about 11.9 MPa. This implied that tensile strength of vulcanized rubbers was independent of molecular weight of the NR employed (Chaikumpollert et al., 2011) . Deproteinized natural rubber (DPNR) has less ageing property than NR because NR contains naturally formed antioxidants which will be removed by deproteinizing. Tangpakadee et al. (1998) degraded DPNR through different radical initiators such as potassium persulfate (KPS), azobisisobutyronitrile (AIBN) and benzoyl peroxide. Better result was obtained by degradation with KPS because of its good solubility in water and latex. Tangpakadee et al. (1998) concluded that during degradation with KPS aldol condensation occurs, in which reactive formaldehyde group will react with carbonyl group. The recombination of carbonyl groups due aldol condensation increase the average number of molecular weight of DPNR. To reduce the effect of aldol reaction several kinds of carbonyl compounds such as acetone, propanal and formaldehyde were added into the reaction mixture (the aldol condensation will occur between degraded DPNR and one of these carbonyl compounds). The rate of depolymerization was faster in presence of carbonyl compound than with the radical initiator alone. The minimum molecular weight was obtained by 1 phr KPS and 15 phr propanal after 5 h of the reaction. To obtain the optimum reaction temperature different temperatures (45º, 60º and 75ºC) were applied. The best yield was achieved at 60ºC. Measurement of particle size distribution and

mean diameter particle size after and before depolymerization shows any changes, which means that the rubber particles are not broken during degradation. The deduction in polydispersity indicate that reaction proceeds randomly to come to equilibrium. During depolymerization reaction primary and secondary hydroxyl group were formed which was confirmed by reduction with $LiAlH_4$ and ^{1}H-NMR analysis. ^{13}C-NMR reveals that both cis and trans epoxide groups are present in degraded product, which indicates that degradation reaction with KPS is a radical reaction (Tangpakdee et al., 1998). Klinkali et al. (2003) obtained LENR with M_n=10000 through degradation of ENR by $(NH_4)_2S_2O_8$ in the presence of propanal. Authors found that the epoxy content does not changed during degradation. The resulting LENR consists different terminal group such as aldehyde and α and β unsaturated carbonyl groups. Due to degradation, a decline in T_g of degraded product was observed (Klinklai et al., 2003). Ibrahim et al. (2014) degraded NR using the combination of H_2O_2 and $NaNO_2$. H_2O_2 could attack double bond and convert it to oxirane ring and $NaNO_2$ act as oxidizing agent and open the epoxy ring, which cause chain cleavage. NO gas is released as by-product during the reaction. It was found that the change in pH of reaction generate LNR with different functional group. In basic condition carbonyl, terminal groups are created, but in acidic condition creation of hydroxyl terminal group is mostly preferred. LNR obtained in acidic condition has lower molecular weight around 10500 after 24 h at 70º C; therefore, degradation at pH below 7 appears to be more effective. The M_n of degraded rubber in basic condition is around 12000 (Fainleib et al., 2013). Ibrahim et al. (2014) reported degradation of NR using H_2O_2 and $NaNO_2$ at temperature of 70ºC in latex phase. The reaction was carried out in an acidic medium. It was observed that a change in ratio of H_2O_2 to $NaNO_2$ affects the reaction yield. The best yield was observed at the ratio of 1:1 H_2O_2 to $NaNO_2$. LNR obtained in this method contains carbonyl and hydroxyl terminal group and achieve a M_n around 24000 after 8 h of reaction in the best condition.

Excessive amount of $NaNO_2$ caused an increase in M_n and polydispersity. By employing higher concentration of H_2O_2 than $NaNO_2$ a decrease in intensity of peak at 3400 cm^{-1} was observed. This peak is assigned to hydroxyl group (Ibrahim & Mustafa, 2014).

2.4.1.5 Other methods

In polymer chemistry metathesis is widely used for polymerization of cyclic olefins to produce cyclic poly (alkenamer) but degradation of unsaturated polymers using this method is also reported (Alimuniar et al., 1990; Ivin, 1983). Metathesis can induce the cleavage and reforming of double bond. This kind of reaction is catalytically induced and could be done by various type of transition metal complexes such as Mo, Re, W with aluminum alkyl compound as co-catalyst. Metathesis includes inter-and intra-molecular reactions which result in degradation and formation of cyclic structure (Phinyocheep, 2014). Alimuniar et al. (1990) reported metathesis degradation of NR using tungsten hexachloride and tetra methyl tin as catalyst. The M_n of degrade rubber decrease from 1.2×10^6 to 1.4×10^4 $gmol^{-1}$. It was observed that a raise in temperature of reaction generate LNR with lower M_n. The drawback of this method is the sensitivity of the catalyst toward impurities therefore, the NR should be purified several times before reaction (Alimuniar et al., 1990). This procedure is further developed to synthesize difunctional telechelic unsaturated polymers with low molecular weight bearing different functional groups such as: boranes, esters, silanes, imide and silyl ether (Chung & Chasmawala, 1992; Marmo & Wagener, 1997). Ultrasound technique has the capability to produce free radicals (hydroxide and hydrogen in water solution) therefore it has been used widely as reaction initiator or for improving the reaction rates of chemical reactions. Ultrasound has been used for degradation of polymers. The

mechanism of ultrasonic degradation is not known exactly. One proposed mechanism suggest that ultrasound radiation produces cavitation bubbles. Formation and break down of these bubbles near the middle of the polymer chain could be the reason of degradation of dissolved polymer. The physical and mechanical properties of cavitation bubbles are related to viscosity, frequencies of the ultrasound waves, diffusion and thermal conductivity coefficiencies (Mauler et al., 1997). Utara et al. (2013) observed a reduction in molecular weight of NR in latex phase by ultrasonic radiation. They found that an increase in frequency of ultrasonic wave from 20 kHz to 25 kHz causes a decrease in M_n of treated rubber. They have also reported that by increasing of latex concentration from 5 to 32 % DRC the M_n of product decreases. As reported by Utara et al. (2013) the structure of degraded NR after sonication remains unaltered. In the best condition M_n of degraded rubber decreases from 2.14×10^6 to 2.38×10^5 after 10 min sonication at 25kHz (Utara & Moonart, 2013).

2.5 Graft polymerization

Besides blending, chemical modification of NR by grafting has been used as a valuable method for improving of properties of NR. Several monomers have been reported for grafting modification of NR including styrene (Kawahara et al., 2006), methyl methacrylate (MMA) (Thiraphattaraphun et al., 2001), dimethylaminoethyl methacrylate (Kangwansupamonkon et al., 2005), maleic anhydride (Nakason et al., 2004a), acrylonitrile (Claramma et al., 1989) and divinylbenzene (Zhou et al., 2001). It has been confirmed by many of the researchers that the most suitable monomers for grafting on NR are styrene and methyl methacrylate (Kochthongrasamee et al., 2006). Grafted natural rubber has better tensile property wettability and biocompatibility (Dafader et al., 2006). The grafting reaction can be carried out in latex, solvent and

solid phase (Hashim et al., 2002). According to polymer morphology there are two kinds of core-shell copolymers: soft core-hard shell and hard core- soft shell (Charmondusit et al., 1998). Grafting of methyl methacrylate to NR results in a soft core-hard shell copolymer which has application as impact modifier. Different initiating systems have been used to graft monomers onto NR including potassium permanganate-ascorbic acid redox system (Nayak & Basak, 1986), tert-butyl hydroperoxide-tetraethylene pentaamine (Arayapranee et al., 2002), benzoyl peroxide, acetylacetonate complex and manganese (Lenka et al., 1985), and potassium persulfate-sodium thiosulfate redox initiators (Kochthongrasamee et al., 2006). Grafting of monomers such as methyl methacrylate into NR often coincides with homopolymerization. The technique of separation of graft copolymer and homopolymer is based on the solubility of the mixture in different solvents. Unreacted rubber could be separated from the mixture with petroleum ether. Generated homopolymer could be extracted using Soxhlet extractor by acetone or alcohol. After each extraction, the grafting efficiency could be determined by residual weight method (Thiraphattaraphun et al., 2001). Graft copolymerization of methyl methacrylate to NR back bone using potassium bromate as initiator was investigated by Lenka et al. To remove the homopolymer, extraction was carried out with benzene. Increasing the concentration of potassium bromate up to a specific amount ($5x10^{-3}$ mol/L) had a positive effect on graft polymerization but further increase reduced the yield of the polymer. It was concluded that higher concentration of potassium bromate facilitates homopolymerization over graft copolymerization. An increase in monomer concentration up to a specific amount (0.1 mol) increases the extent of polymer and there after it decreases. This is due to homopolymerization has occurred by increasing of monomer concentration. Solvent has an important effect on MMA grafting. The best yield was observed by aprotic polar solvent such as DMSO

(Lenka et al., 1985). The order of solvents if grafting efficiency is concerned was found to be:

DMSO>DMF>Dioxane>Benzene>Chloroform

The effect of solvents on grafting yield was justified by different capability of solvents to swell the rubber as well as the ability of solvents to form solvent radical from the primary radicals generated by initiators. The yield of copolymerization changed by using different monomer and the best results in order to reactivity of monomers and grafting yield follows the following sequence:

methyl methacrylate > ethyl acrylate > butyl acrylate > methyl acrylate >ethyl methyl acrylate > acrylonitrile.

Grafting of methyl methacrylate monomer onto NR using potassium persulfate as initiator was reported by Thiraphattarapun et al. (2001). They reported that the grafting increased with increase in initiator concentration to a determined amount; furthermore, increase of initiator will produce abundance free radicals which recombine together and does not affect the conversion speed. They found that homopolymerization overcome graft polymerization at initiator (KPS) concentration more than 0.75 phr. By increasing monomer concentration up to 100 phr the grafting yield increased; and further increase in monomer concentration homopolymerization prevailed as had been reported before by Lenka et al. (1985) whereby KPS decomposed at higher temperature so the conversion increased by rising of temperature, but at temperature greater than 55ºC the grafting efficiency decreased due to homopolymerization. After 8 h of reaction the maximum level of grafting efficiency was achieved. By prolonged reaction time due to decreases of active grafting site, a deduction in grafting reaction could be observed. Grafting of NR with MMA in latex stage is a core shell type copolymerization in which

NR acts as core and MMA as shell. The grafting reaction of NR occurs largely at the surface of NR because dissolved KPS in water could not diffuse inside the rubber chains. NR seeds show a spherical morphology which was surrounded by a thin layer of PMMA as a graft copolymer (Suksawad et al., 2011). Preparation of thermoplastic elastomer from NR by graft copolymerization of styrene monomer in latex stage was reported by Suksawad et al. (2011). Tert-butyl hydroperoxide and tetraethylenpentamine were used as initiator system. They found that the appropriate concentration of initiator to achieve best grafting efficiency depends on monomer concentration and there is no linear relation between monomer and initiator concentration. For example, the best grafting efficiency at a monomer concentration of 1.5 (mol/kg rubber) was observed by initiator concentration of about 3.3 $x10^{-2}$ (mol/kg rubber). By increasing of monomer concentration to 5.5 (mol/kg rubber) the best efficiency was observed by employing $20x10^{-2}$ (mol/kg rubber) of initiator. It was demonstrated that grafting efficiency plays a vital role in mechanical properties of obtained graft copolymer. For example, only graft copolymers with grafting efficiency higher than 60 mol% could have a tensile strength greater than 20 MPa (Suksawad et al., 2011).

2.6 Coating

2.6.1 General information

There are two main reasons for applying coating which is for corrosion prevention and decorative purposes. Most metals are produced by reducing ores. If metals are exposed to the atmosphere they have the tendency return to their original chemical structure. This process is called corrosion. Applying coating prevents

corrosion of metals for a period of time. There are two main kinds of coatings including organic and inorganic coatings. Protection of coated metals could be done either by barrier action of the coating or active corrosion inhibition. Barrier property of a coating acts by preventing diffusion of water and oxygen to the surface of metal and by resistance inhibition. Barrier properties is a limited property and depends on the chemical and physical structure of the resin used for preparation of coating. By increasing of hydrophobicity of a resin, the permeability to water decreases but all binders are permeable to water and oxygen in some extent. The diffusion rate of water for some coating is shown in Table 2.2 (Mansfeld, 1986). Resistance inhibition provided by coating is accomplished by preventing of charge transfer due to an increase in the electrical resistance.

Table 2.2: Diffusion Data for Water through Organic Films.

Polymer	**$Dx10^9$ (cm^2/sec)**
Epoxy	2-8
Phenolic	0.2-10
Polyethylene (low density)	230
Poly(methyl methacrylate)	130
Poly(vinyl acetate)	150
Poly(vinyl chloride)	16
Vinylidene chloride/acrylonitrile copolymer	0.32

Most of the coatings contain three basic ingredients, i.e. pigment, binder and solvent. Pigments are insoluble in coating. They have decorative and in some extent protective properties. Extenders are pigments which do not provide color and can carry

out very important functions such as increasing the water impermeability, enhancing the adhesion and improving the hardness of the coating. Binder could be a resin which is a polymeric material. Binders cover and protect the surface and bind and hold other parts of coating together. Solvents provide the fluidity of the coating which is necessary for penetration into the intricate crevices (Bentley & Turner, 1997). In general, there are two types of resins namely thermoplastic and thermosetting resins. Thermoplastic resins have very high M_n and are capable to form film without any need of chemical reaction. Film formation of thermoplastic resin involves the evaporation of solvent. In contrast, thermosetting resins have usually low M_n and after application due chemical reaction the M_n of resin increases and film formation occurs. The curing reaction is done by formation of strong chemical linkage between the polymer chains. Therefore, thermosetting resin should have reactive functional groups and an added curing agent. The reaction between resin and curing agent (cross-linkage) begins after the coating is applied. There are several types of resins as shown in Table 2.3 (Mannari & Patel, 2015).

Table 2.3: Typical examples of resin types.

Resin type	Examples	Film formation	Application
Thermoplastic resin	Thermoplastic acrylic resin	Physical drying	Acrylic coatings, wood finishes
	Acrylic latex	Coalescence	Architectural coatings
	Nitrocellulose resin	Physical drying	NC refinishes, nail lacquers
Thermosetting resin	Alkyd resin	Air oxidation	Architectural coatings
	Epoxy resin	Crosslinkers, amines, acids	Industrial coatings, anticorrosive coatings
	Polyurethanes	Crosslinkers, moisture	Industrial coatings, wood finishes

	Polyesters	Crosslinkers, co-curing resins	Industrial coatings
	Acrylate functional	UV curing	Coatings, printing inks

2.6.2 Epoxy resin

One of the most important resins utilized in paint industry is epoxy resin. Epoxy resins are very reactive and have at least two oxirane groups per molecule. Oxirane could react with both nucleophiles and electrophiles. Diglycidyl ethers of bisphenol A (DGBA) is the most widely used epoxy resin (Figure 2.12). DGBA is condensed from epichlorohydrin (1-chloro-2,3-epoxypropane) and bisphenol A [2,2-bis-(4 hydroxyphenyl) propane].

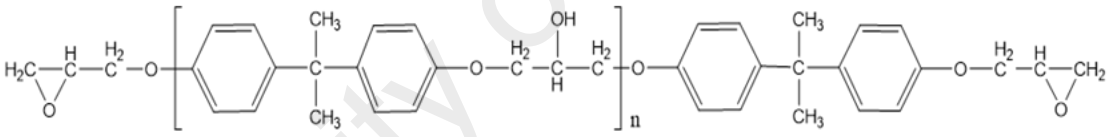
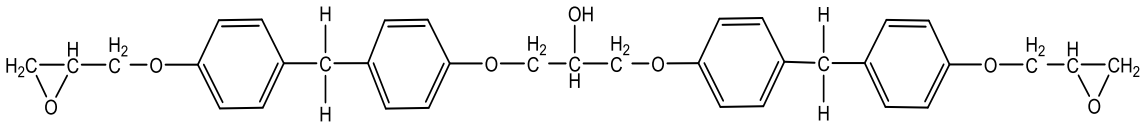


Figure 2.12: Chemical stucture of DGBA epoxy resin.

Another type of commercial epoxy resin is bisphenol F resin. Bisphenol F based epoxy resin has lower viscosity than bisphenol A and provide better solvent, acid and chemical resistances (Figure 2.13). Bisphenol F based epoxy resin is condensed from epichlorohydrin and bisphenol F. This kind of resin, due to its lower viscosity is used in



highly filler loaded and solvent-less coatings (Ellis, 1993).

Figure 2.13: Chemical structure of bisphenol A based epoxy resin.

Epoxy Novalac resin is produced by reaction of phenol-formaldehyde resin and epichlorohydrin. Epoxy Novalac resin in contrast to the last two resins has more than two functional epoxy groups per molecule. Because of the multi-functionality, this kind of resin forms films with higher crosslink density and therefore has excellent solvent and chemical resistances. Epoxy Novalac has better thermal resistance because of the presence of large quantity of aromatic rings in the structure. (Brock et al., 2000). Epoxy resin could almost be cured by chemical reaction. There are several types of curing agents including aliphatic amines, aromatic amines, polycarboxylic acids, polycarboxylic anhydrides, phenol-formaldehyde resins, amino-formaldehyde resins and mercaptans (Brock et al., 2000). Table 2.4 shows the world market usage for different types of curing agents in 2009.

Table 2.4: The estimated world market usage for different types of curing agents.

Curing agents	**Relative use(%)**
Amines(aliphatics)	10
Amines(cycloaliphatics)	7
Amines(aromatics)	3
Amines(dicyandiamine)	2
Polyamides	16
Polyamidoamines	7
Phenol-and amino-formaldehyde resins	16
Carboxylic acid functional polyesters	22
Anhydrides	12
Polysulphides and polymercaptans	3
Catalysts	2
Total	100

Low molecular weight aliphatic polyamines exhibit the highest reactivity with epoxy resin but they suffer from some drawbacks such as toxicity, unpleasant odour and high evaporation rate. These problems could be lighten by pre-reacting low molecular weight polyamines with a small amount of epoxy resin component; to increase the molecular weight. The remaining NH bonds are able to react with epoxy resins when the curing agent is mixed with the second part of the coating. This kind of hardener is known as polyamine adduct hardener (Brock et al., 2000). Polyketimines are another primary amine which are blocked by ketones. The deblocking takes place by action of moisture on the applied wet film. Polyamidoamines are a very important type of amine hardener. Polyamidomines could be synthesized by reaction between dimerized fatty acid with an excess of diamine (Brock et al., 2000). Polycarboxylic anhydrides are the second most important type of hardeners after amines. They could react at elevated temperature with hydroxyl groups that exist in the chemical structure of the epoxy resin as well as with oxirane groups to some extent. This hardener is widely used in epoxy powder coatings. Epoxy coatings cure with polyanhydrides are resistant to chemicals while they are flexible and adhere well to metallic substrate (Mark, 2004).Epoxy resin could be derived by oxidation of unsaturated resin using peracid as reagent. A major advantage of this kind of epoxy resin is the absence of aromatic ring present as in bisphenol A and bisphenol F. The aromatic ring increases the UV absorption of the resin and initiates degradative process by formation of conjugated structure. Therefore, resin free of aromatic compounds has better weather resistance (Atherton et al., 1982). There are not many reports about ENR used as coating. Jorge et al. cured ENR with 25 mol% epoxide using a trifunctional thiol (trimethylolpropane tris(2-mercaptoacetate)). Thiols could readily react with epoxide group at ambient temperature (Lee et al., 1963). FTIR spectrum of the cured film showed the disappearance of epoxide ring peak at 870

cm^{-1}. It was observed that the cured film has better tensile strength as well as thermal and swelling properties (Jorge et al., 2010).

CHAPTER 3: MATERIALS & METHODS

3.1 Materials

Potassium peroxodisulfate ($K_2S_2O_8$) and disodium hydrogen phosphate was obtained as extra pure chemicals from Hamburg Chemical GmbH. Tetrahydrofuran (THF), acetic acid (glacial 100%), 2-butanone (MEK), potassium hydrogen phthalate, chlorobenzene, petroleum ether and toluene were reagent grade chemicals from Merck. Periodic acid was purchased from Fischer Scientific. Potassium permanganate ($KMnO_4$), benzophenone, acetone and ethanol were reagent grade chemicals from R&M Chemicals. Hexamethyldiamine 98% was obtained from Sigma Aldrich. ENR 25 (ENR) and Natural rubber (NR) used was SMR 20 (SMR, Standard Malaysian Rubber), a kind gift from Rubber Research Institute of Malaysia (RRIM). ENR25 is an epoxidized natural rubber with 25 mol % epoxidation.

3.1.1 Preparation of ENR 25 solution

ENR 25 was mechanically masticated using a laboratory two- roll mill at a roll speed of 5.2 (cm sec^{-1}). The roll diameter was 4 cm and the nip gap was adjusted to 0.2 mm with the nip setting of 4 mm for 3 times. The masticated rubber was used for preparing of following solution:

3.1.1.1 ENR 25 solution (13.4 % w/w) in MEK

The masticated ENR 25 was then weighed and introduced in a reaction vessel. MEK was added to make up the concentration equal to 13.4 % w/w. The solution was stirred with a mechanical stirrer at a speed of 1000 rpm until ENR 25 is dissolved.

3.1.1.2 ENR 25 solution (5.6% w/w) in THF

The masticated ENR 25 was then weighed and introduced in a reaction vessel. THF was added to make up the concentration equal to 5.6 % w/w. The solution was stirred with a mechanical stirrer at a speed of 1000 rpm until ENR 25 is dissolved.

3.2 Different degradation methods to produce LENR

3.2.1 Mechanical breakdown of ENR25

ENR25 (5 g) was milled used a laboratory two- roll mill at a roll speed of 5.2(cm sec^{-1}). The roll diameter was 4 cm and the nip gap was adjusted to 0.2 mm. One sample of ENR25 was milled for 3 h and a second sample was milled for 8 h. After milling, the sticky LENR was dissolved with toluene from the rollers and collected into a beaker, and toluene was removed by vacuum distillation at 40 ºC.

3.2.2 Oxidative degradation initiated by potassium peroxodisulfate.

74.6 g of dissolved ENR 25 in MEK (13.4% w/w) was charged into a reaction vessel. Potassium peroxodisulfate (6.4 g) and disodium hydrogen phosphate (8.9 g)

were dissolved in 27 ml water and then it was added drop-wise to the ENR solution. The reaction was carried out at 60 º C. A flow of air was pumped to the solution during mixing with an overhead stirrer. After the specific reaction time, the solution was cooled down and the degraded ENR was coagulated by adding methanol and washed several times with water. The obtained liquid rubber was dried in a vacuum oven at room temperature.

3.2.3 Photo-oxidation with UV radiation.

Two methods were used for degradation by UV radiation. There were two differences between these methods. The first one was the intensity of UV irradiation which was increased by approaching the UV lamp to the ENR solution and the second one was the concentration of ENR solution utilized. The two methods are described as follows:

3.2.3.1 Method A:

A UV lamp, Dymax 5000 EC, supplies radiation at 365 nm (λ) and intensity of 225 mW/cm^2. ENR25 (15 g) was dissolved in toluene (135 g) and introduced in a beaker which was stirred with a magnetic stirrer during irradiation. The UV lamp was located 30 cm above the beaker and a fan cooled the set up during irradiation. The lamp was switched on for 30 min and off for 30 min. During the UV irradiation, the temperature of rubber solution did not go over 50ºC. After different radiation time the solvent was evaporated off under reduced pressure at 40ºC and the products were analysed with FTIR, NMR and GPC.

3.2.3.2 Method B:

A solution of 15 g ENR 25 dissolved in 165 g toluene was prepared. The ENR 25 solution was charged into a beaker and was stirred with magnetic stirrer. A UV lamp, DYMEX 5000 EC supplies radiation with wave length 365 nm and intensity of 225 mW/cm^2. The lamp was switched on for 30 min and off for 30 min. The UV lamp was located around 15 cm above the solution. The setup was carefully covered with aluminium foil and cooled with a fan during reaction. At the specified time of irradiation, the solvent was removed under reduced pressure at room temperature. The experiment was repeated with 1, 3, 5, 7, 10, 14 and 18 h of irradiation time. To investigate the effect of epoxide group on the degradation, NR is also degraded under the same conditions as ENR by this method.

3.2.4 Oxidative degradation with potassium permanganate

Degradation was carried out in a reaction vessel equipped with a mechanical stirrer. Initially the vessel was charged with 169 g of ENR25 solution in THF (5.9% w/w). $KMnO_4$ (10 g) was dissolved in a mixture of 160 g water and 11.4 g acetic acid. The dissolved ENR was mixed with various amounts of mentioned $KMnO_4$ solution: e.g. 0.026, 0.044, 0.075 and 0.145 mol of $KMnO_4$ per hundred grams of rubber (mphr) as is shown in Table 3.1. Samples of the reaction solution were withdrawn after 1, 3, 5, 10 and 18 h respectively. After filtering samples were coagulated by adding methanol and washed several times with water. The obtained liquid rubber was dried in a vacuum oven at room temperature. The same procedure was used for degradation of NR.

Table 3.1: Amount of each variable reactant added to the reaction mixtures for degradation with $KMnO_4$.

Composition	Sample 1 0.026 (mphr)	Sample 2 0.044 (mphr)	Sample 3 0.075 (mphr)	Sample 4 0.145 (mphr)
ENR 25 (g)	10	10	10	10
KMnO4 (g)	0.41	0.69	1.18	2.29
Water (g)	6.56	11.12	18.96	36.65
Acetic acid (g)	0.47	0.79	1.35	2.61

3.2.5 Oxidative degradation with periodic acid

169 g of dissolved ENR 25 in THF (5.9% w/w) was charged into a reaction vessel. Periodic acid was added to the stirred mixture with various amounts: e.g. 0.026, 0.044, 0.075 and 0.145 mole per hundred grams of rubber (mphr) as is shown in Table 3.2. The mixture was stirred at 30 ºC. Samples of the reaction solution were withdrawn after 1, 3, 5, 10 and 18 h and filtered to remove iodic acid then the rubber was precipitated by adding 800 ml methanol and washed several times with water, thereafter there were dried at room temperature in a vacuum oven. To investigate the effect of epoxide group on the degradation, NR is also degraded under the same conditions as ENR by this method.

Table 3.2: Amount of each variable reactant added to the reaction mixtures for degradation with H_5IO_6.

Composition	Sample 1 0.026 (mphr)	Sample 2 0.044 (mphr)	Sample 3 0.075 (mphr)	Sample 4 0.145 (mphr)
ENR 25 (g)	10	10	10	10
H_5IO_6 (g)	0.41	0.69	1.18	2.29

3.3 Graft polymerization

Methyl methacrylate was grafted onto LENR obtained from UV photo oxidation method A, with M_n of 11485 after 6 h radiation which is coded LENR6 (Table 4.6). Graft polymerization was carried out in a flat bottom reaction flask equipped with a magnet stirrer. LENR6 (10 g) was dissolved in toluene (26 g). Thereafter, the flask was charged with LENR6 solution. Methyl methacrylate was treated with 2 w/v % NaOH solution to remove inhibitor and subsequently washed with deionized water and dried over anhydrous $CaCl_2$ prior to usage. Methyl methacrylate, and benzophenone in specific amount was added to the solution. The amount of each variable reactant added to the reaction mixtures is shown in Table 3.3. Then, the mixture was deoxygenated by purging with nitrogen gas. The flask was sealed and a UV lamp was located 30 cm above it. After one hour irradiation, the solvent was evaporated and Soxhlet extractor was used to wash out ungrafted LENR by petroleum ether at temperature between 60-80 ^oC for 24 h. The homopolymer (PMMA) was removed by extracting the residue by acetone/ethanol (85/15 v/v) mixture with Soxhlet extractor as described before.

Table 3.3: Amount of each variable reactant added to the reaction mixtures.

Composition	Sample 1	Sample 2	Sample 3
LENR (g)	50	50	50
Toluene (g)	78	78	78
MMA (g)	40	40	40
Benzophenone (g)	0.25	0.42	0.57

3.4 Characterization Methods

3.4.1 ^{1}H-NMR spectroscopy

To determine molecular structure of samples, nuclear magnetic resonance spectroscopy operating at 270 MHz on a JNM-GSX270 Fourier Transform Spectrometer with deuterated chloroform as a solvent was used. The concentration of the sample in deuterated chloroform solution was 1-5 w/v%. The ratio of olefinic methine proton to oxirane methine proton was calculated based on the equation 3.1.

Ratio of olefinic methine proton to oxirane methine proton $=\left(\frac{A_{5.14}}{A_{2.68}}\right)$ [3.1]

Where, *A* is integrated area of the signals and subscript numbers represent chemical shift (ppm).

3.4.2 FTIR spectroscopy

FTIR spectra were recorded on a Perkin Elmer FTIR RX1 spectrometer at room temperature, with 4 scans from 4000 to 400 cm^{-1} and resolution of 4 cm^{-1}. To minimize the effect of non-uniform film thickness, ENR was dissolved in toluene in a fixed concentration. A constant quantity of the solution was put onto a NaCl cell, and the solvent removed by a hot air blower.

3.4.3 Gel Permeation Chromatography (GPC) analysis

Gel permeation chromatography is a powerful technique used separation method to characterize polymers. Separation by GPC occurs according to hydrodynamic volume and not according to molecular weight. Hydrodynamic volume is determined using a concentration sensitive detector and a calibration curve. The hydrodynamic volume of the sample could be related to that of the standard samples using Mark-Houwink-Sakurada relation (Gaborieau & Castignolles, 2011). The molecular weights of the samples were determined using gel permeation chromatography (GPC Model 305 TDA Viscotec Houston), with a differential refractometer at λ=660 nm (RID 3580). The column was calibrated using monodispersed polystyrene standards. Tetrahydrofuran was used as eluent at a flow rate of 1 ml min^{-1}. The Samples were dissolved in THF under 24 h of shaking with a concentration about 0.2-0.4 mg/ml. Prior to analysis the samples were filtered through 0.45 µm syringe filter.

3.4.4 Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry in polymer science is widely used for determination of glass transition temperature. During a polymer matrix pass from glassy to rubbery state a rise in specific heat could be observed. By heating of a polymer beyond the T_g, chain mobility becomes easier therefore, the polymer becomes flexible. The transition from glassy to rubbery state doesn't occur at one unique temperature but rather over a range of temperatures. DSC thermograms in nitrogen atmosphere were obtained with a Mettler Toledo DSC-822e DSC analyser equipped with a sub-ambient cooling accessory (HAAKE EK/90, Mettler Toledo). The DSC machine was calibrated using high purity indium before each measurement to ensure accuracy. Approximately 5−10 mg of sample was encapsulated in an aluminium pan and sealed. The sample was

analysed by heating from -60 °C to 80 °C at a scan rate of 20 °C/min. T_g was defined as the middle point of the inflection in the DSC curves.

3.4.5 Determination of Epoxy content by direct titration method

Epoxy content of ENR and LENR was determined by titration method. Known weight of rubber was dissolved in chlorobenzene. The solution was titrated with standardized hydrobromic acid in glacial acetic acid, using crystal violet indicator. This method was developed by Durbetaki (1956). Burfield & Gan (1975) realized that this method was relevant for determination of epoxy content of ENR. The reagents mentioned above were prepared as follows:

a) Known weight of sample was introduced into an Erlenmeyer flask. The sample was dissolved in 50 ml of chlorobenzene.

b) For preparation of crystal violet indicator solution 0.1 g of crystal violet was dissolved into 10 ml glacial acetic acid into an Erlenmeyer flask.

c) A solution (0.1N) of hydrogen bromide was prepared by dissolving of 6.33 g HBr (32% in acetic acid) in 250 ml of glacial acetic acid.

d) 5 g of potassium hydrogen phthalate (KHP) was dried in the oven at 110 ºC for 2 h. The KHP solution was prepared by dissolving of 0.4 g KHP in 10 ml of glacial acetic acid into an Erlenmeyer flask. After dissolving, 5 drops of crystal violet indicator was added into the flask titrated with 0.1 N HBr solution in a burette to get a blue green end point. The normality of HBr solution was calculated as follows:

$$N = \left(\frac{W \text{ X } 1000}{204.2 \text{ X } V}\right) \qquad [3.2]$$

Where: W is the weight of KHP, g, used and V is HBr solution used, ml.

e) 5 drops of crystal violet indicator solution was added to sample solution and then it was titrated with HBr solution to get a blue green colour endpoint.

f) A blank sample was prepared by adding 5 drops of crystal violet indicator in 50 ml of chlorobenzene into an Erlenmeyer flask. The blank sample was titrated in an identical manner.

g) The epoxy content, E, in gram equivalents of oxirane groups per 100 g of sample was calculated as follows:

$$E=\left(\frac{N(V-B)}{10 \text{ X } W}\right) \qquad [3.3]$$

Where: N is normality of the HBr solution, V is HBr solution used for titration of sample, ml, B is HBr solution used for titration of blank sample, ml and W is the weight of sample used, g.

3.5 Preparation of coating based on grafted LENR

3.5.1 Grafted LENR

The epoxy content of grafted LENR (GLENR2) was measured by the method explained in section 3.4.5. The T_g of obtained grafted LENR was measured by DSC method. The typical properties of GLENR2 are shown in Table 3.4.

Table 3.4: Properties of grafted LENR (GLENR2).

Property	Value
Appearance	Light yellow transparent
Epoxide equivalent weight (g/eq)	440
T_g (ºC)	42.8

3.5.2 Curing agent

Three types of hardener were used to react with grafted LENR (GLENR2). The three-selected hardener are (i) Aradure 943 a solvent free aliphatic polyamine adduct (from Huntsman), (ii) Epikure F 205 a cycloaliphatic amine (from Hexion Specialty Chemicals Inc.) and (iii) hexamethylenediamine a difunctional aliphatic amine (from Sigma Aldrich). The properties of hardeners are shown in Table 3.5.

Table 3.5: Properties of curing agents.

Property	Aradure 943	Epikure F205	Hexamethylene diamine
Appearance	Brown liquid	Yellow liquid	Clear liquid
Density at 25ºC (g/ml)	1.08	1.04	0.89
H^+ Active equivalent weight (g/eq)	38	102-106	29
Molecular weight (g/mol)	-	170	116
Flash point (ºC)	93	117	94

3.5.3 Treatment of iron panel

The surface of iron panels was abraded with sand paper No.400 and No.600. To remove the dust from the abrasion the panels were wiped off with a wet cotton cloth for several times. Thereafter, the surface was wiped again with wet cloth soaked in toluene-propanol (50/50 v/v) mixture. The prepared panel were stored in drying cabinet prior to usage.

3.5.4 Preparation of coating mixture

Three different mixtures of grafted LENR(GLENR2) with the mentioned hardener were prepared with the following stochiometric ratio:

Aradure 943: > 100g GLENR2 ⟶ 8.63 g Aradure 943 curing agent.

EpikureF205: > 100g GLENR2 ⟶ 23.63g Epikure F205 curing agent.

Hexamethylenediamine: > 100g GLENR2 ⟶ 6.59g Hexamethylenediamine curing agent.

The prepared coating mixtures were diluted with toluene-MEK (70/30 w/w) mixture and stirred until they become homogenous. Coating mixtures were applied on iron panels using Sheen Coater (Model S971096) with a wet film thickness of 100 µm. The coated panels left to dry at room temperature for 6 days before testing.

3.5.5 Determination of film properties

3.5.5.1 Drying time test

In order to determine drying time the testing method stated in ASTM D1640-83 was used. Set-to-touch time is the time the wet film does not stick to finger. With the tip of a clean finger the coated film was gently touched and placed a piece of clean glass. Dry-to-touch is reached when the film no more sticks to finger and does not rub up when the finger is lightly moved across the surface. To determine dry-hard time a maximum pressure of the thumb is applied on the film. If no marking is observable on the contacted area the dry-hard time is reached.

3.5.5.2 Adhesion test

Adhesion test was done according to testing method stated in ASTM D3359-93. A hatch consisting of 6 cuts in each direction (horizontal and vertical) was carved with space of 1 mm and length of 20 mm. Thereafter the film was brushed gently. A self-adhesive tape was placed and rubbed on the hatch area. After 90 second the tape was removed in an angle close to 180º C. The hatch area was interpreted for any paint removal. The adhesion was determined according to Table 3.6.

Table 3.6: Classification of adhesion test results.

Classification	Surface of cross-cut area from which flaking has occurred. (Example for six paralleled cuts)	Remarks
5B	None	The edges of the cuts are completely smooth; none of the squares of the lattice is detached. Good and acceptable
4B		Small flakes of the coating are detached at intersections; less than 5% of the area is affected. Good and acceptable.
3B		Small flakes of the coating are detached along edges and at intersection of cuts. The area affected is 5 to 15 % of the lattice. Good and acceptable
2B		The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice. Not acceptable.
1B		The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65% of the lattice. Not acceptable.
0B	Greater than 65%	Flaking and detachment worse than Grade 1B. Not acceptable.

3.5.5.3 Pencil hardness

To determine scratch hardness, pencil hardness method was used according to ASTM D3363-92a. A set of 14 standard pencil with scale of hardness 6H hardest to 6B softest was obtained. The pencil was inserted into pencil tester. The pencil tester was moved over the surface of coating with a fixed angle of 45º and a fixed pressure of 750 g (Figure 3.1). The test was repeated until two pencil consecutives in term of hardness was found, one which could scratch the surface of coating and another which is not capable to indent the film. The hardest pencil grade which fails to scratch the coating was recorded.

Softer: 6B- 5B- 4B- 3B- 2B- B- HB- F- H- 2H- 3H- 4H- 5H- 6H: Harder

Figure 3.1: Pencil hardness kit

3.5.5.4 Water resistance and alkali resistance

The resistance of coating against immersion in water was determined according ASTM D1647-89 and the reported procedure by Taylor et al. (Taylor & Marks, 1972). The coated panel was placed into a beaker. Distilled water was introduced into the beaker. After 18 h the panel was removed and the film condition was evaluated. The defects including whitening, shrinkage, film softened, loss of glass and lift off was reported. Coated panels were immersed in NaOH (0.5N) aqueous solution for 8 h. Thereafter, the panels were taken out and inspected for any defect following the same procedure as that of water resistance.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Study of three degradation methods to produce LENR through radical mechanism

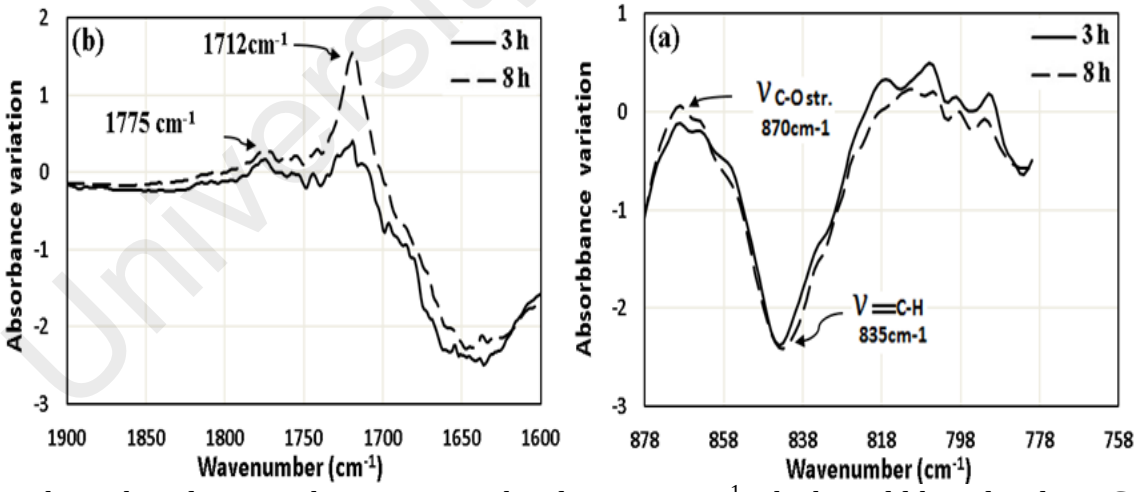
4.1.1 Introduction

In this part three degradation methods are compared including (i) mechanical milling, (ii) oxidative degradation initiated by potassium peroxodisulfate and (iii) photo-oxidation initiated by ultra violet (UV) irradiation. The mechanism of these three methods is assumed to involve radical attack either to the double bond (addition mechanism) or to hydrogen atom in the allylic position which leads to abstraction of the hydrogen atom.

4.1.2 Degradation using a roll mill

The mechanical breakdown by mastication occurs because long chain molecules break by action of stress. The shearing forces acting on rubber during mastication, first overcoming intermolecular forces in bulk deformation of rubber and then cause rupture of primary bonds of rubber chain with length greater than a critical value so it becomes extended and breaks at a band located in the central section between chain segments. But chain length shorter than critical length could not be broken. If oxygen is present it reacts quickly with the free radicals and ultimately lead to formation of lower molecular weights. If mastication undergoes without oxygen under an inert atmosphere, radicals recombine together and this could lead to production of more branching and

crosslinking (Pike & Watson, 1952). One sample of ENR 25 was masticated for 3 h and a second sample was milled for 8 h. The subtraction of the initial spectrum of ENR25 from the IR spectra of the products after different milling times allows the observation of several changes during milling. The subtracted IR spectra (Figure 4.1) in the double bond region (=C─H 835 cm^{-1}) shows a decrease in double bond density within the first 3 h but subsequently there is no further reduction in double bond. Table 4.2 shows the change in the ratio of A_{835}/A_{2962} of IR spectrum after 3h and 8 h of mastication. The absorption peak at 2962 cm^{-1} belong to C-H str. of methyl group which is not affected noticeably. The methyl group is one of the most populous unit in the ENR structure which does not take part noticeably in degradation reaction; therefore, it was selected as the internal reference. The ratio of other peaks to 2962 cm^{-1} can show the changes occurring during reaction. Figure 4.2 shows the subtracted IR in the region of 2962 cm^{-1} by the various degradation methods. The absorbance peak of the C-H str. of methyl group remained more and less unchanged during the degradation. The IR spectrum in



the carbonyl region shows a rise in band at 1712 cm^{-1} which could be related to –C=O of unsaturated ketone (Figure 4.1and Table 4.1). Two shoulders appear also at 1735 cm^{-1} and 1775 cm^{-1} which can attribute to ester and lactone respectively (Piton & Rivaton, 1996).

Figure 4.1: (a) Changes in subtracted IR spectra in the carbonyl vibration region after 3 & 8 h mastication; (b) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}).

Table 4.1: Absorbance ratio in the double bond and carbonyl region to C-H stretching of methyl group after mastication.

Reaction time(h)	A_{835}/A_{2962}	A_{1712}/A_{2962}	A_{1738}/A_{2962}	A_{1775}/A_{2962}
0	0.9163	0.7608	0.7621	0.7539
3	0.8966	0.7614	0.7622	0.7549
8	0.8975	0.7731	0.7691	0.7611

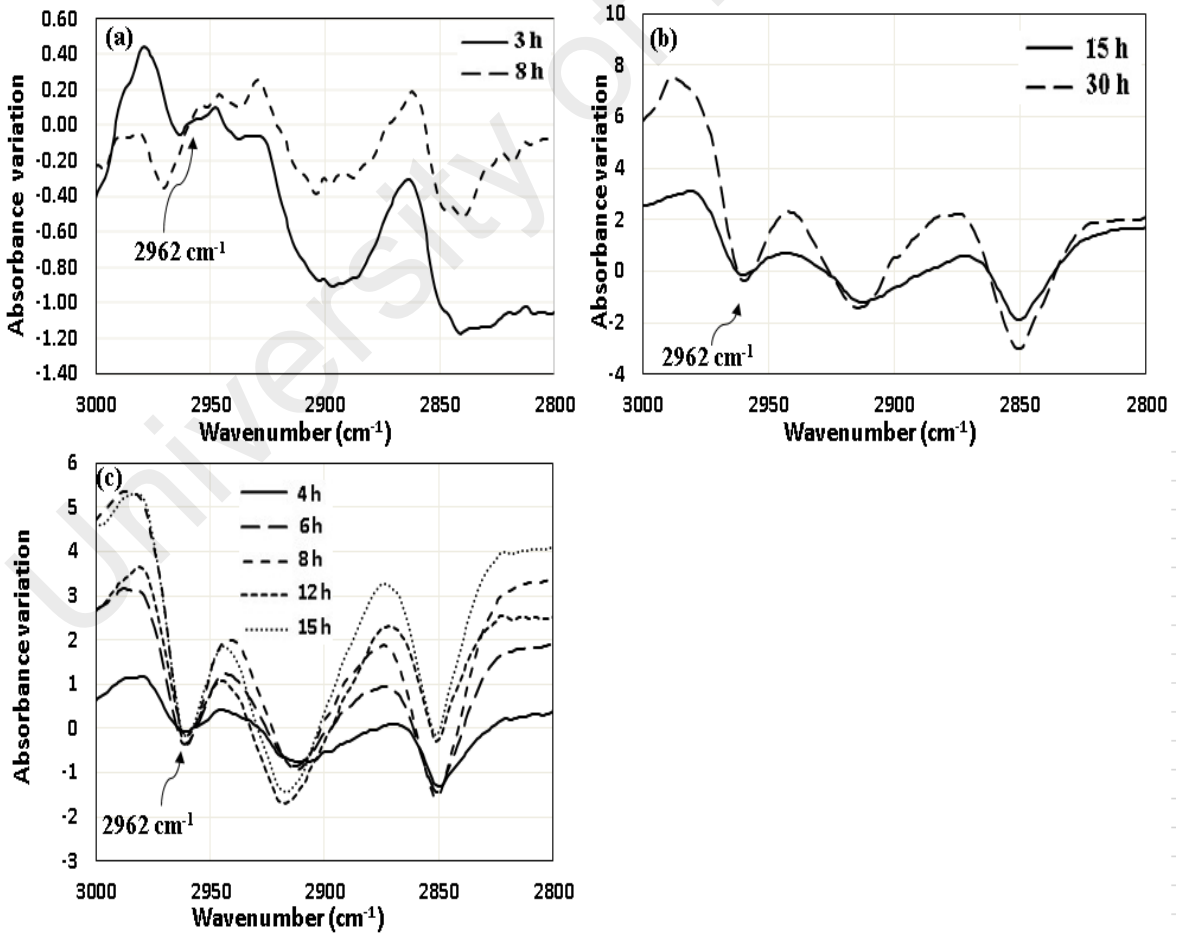


Figure 4.2: Changes in subtracted IR spectra in the region of 2962 cm^{-1} in different degradation methods. (a) mastication; (b) degradation with $K_2S_2O_8$; (c) degradation with UV.

The ^{1}H-NMR spectra do not show many changes between the ENR25 before and after mechanical mastication (Figure 4.3). A small peak appears at 9.7 ppm which could be assigned to aldehyde and another peak at 3.64 ppm (s, $CH_2COOC\boldsymbol{H_3}$) which could be related to ester group. The spectra show a peak at 0.85 ppm which can be attributed to terminal methyl group. The divided integration area of the signals at 5.1 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) shows a s decrease of double band after 3 h milling (Figure 4.4). Both the M_n and M_w decrease during milling as shown in Table 4.2.

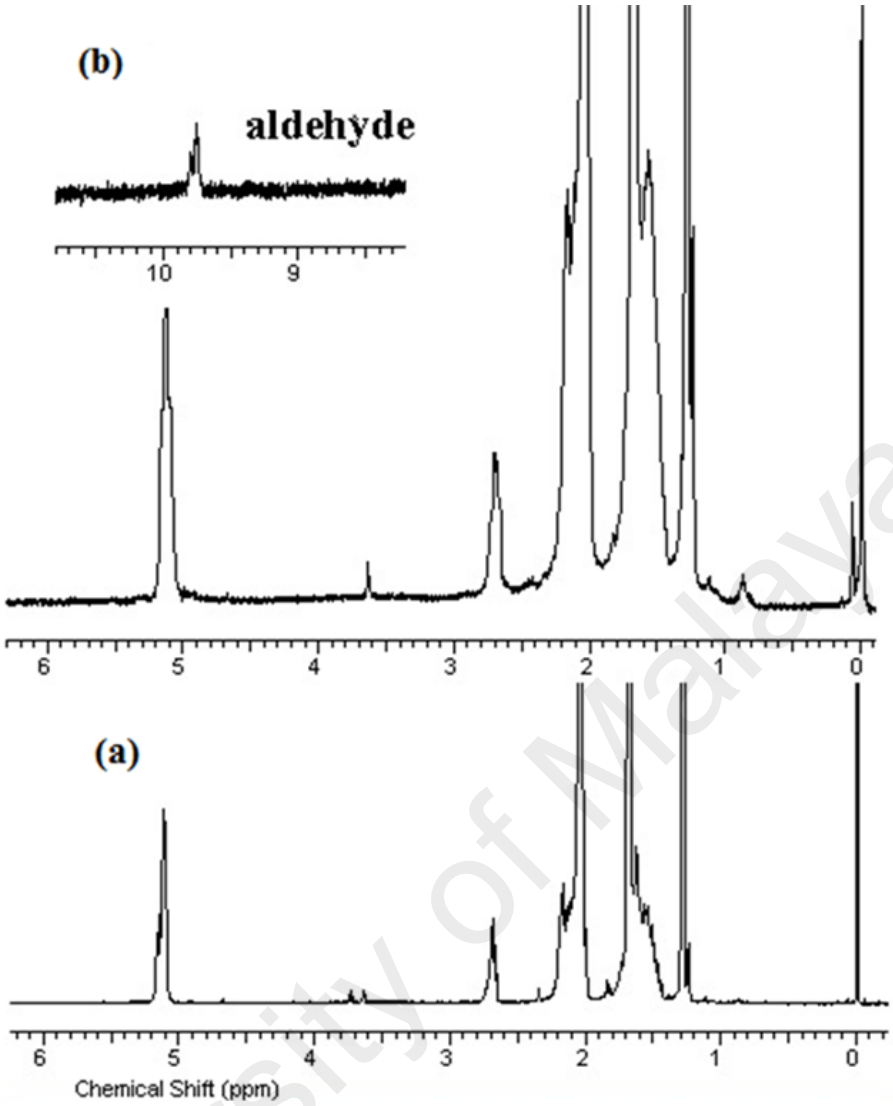
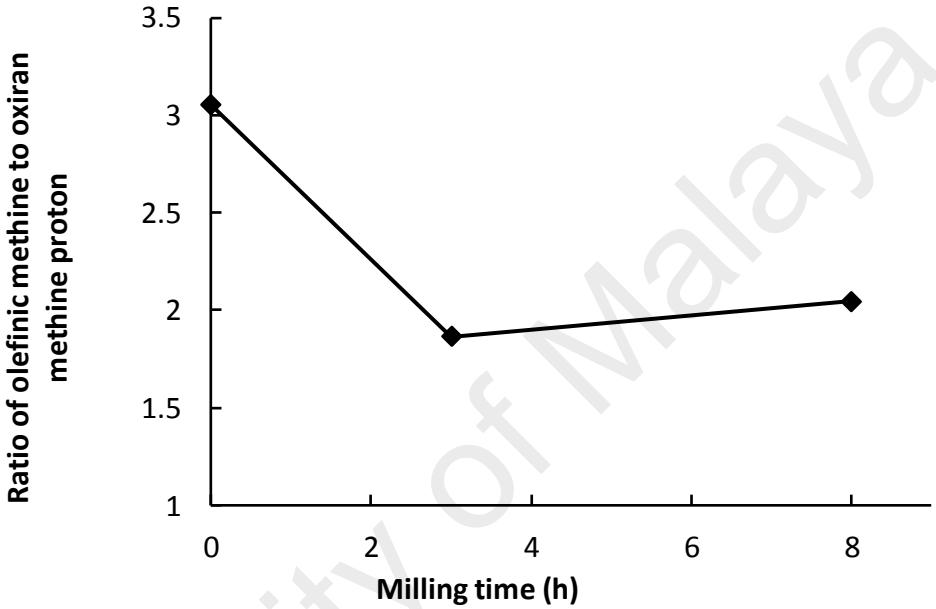


Figure 4.3: ^{1}H- NMR of (a) ENR25; (b) LENR produced after 8 h mastication.

Table 4.2: Results of average molecular weight and polydispersity index after milling.

Milling time (h)	M_n	M_w	PDI
0	148391	695508	4.68
3	21962	63622	2.9
8	11623	40762	3.5

Figure 4.4: Ratio of integration area of the signals at 5.1 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton).



4.1.3 Degradation using potassium peroxodisulfate

The reaction of ENR with $K_2S_2O_8$ as a radical initiator was carried out at two different reaction times of 15 and 30 h. Thermal activation can induce persulfate ($S_2O_8^{2-}$) degradation to form sulfate radicals ($SO_4^{-\circ}$). The sulfate radicals are one of the strongest oxidizing species with a redox potential estimated to be 2.6 V similar to that of the hydroxyl radicals (Roshani & Leitner, 2011). The sulfate radicals are more stable than hydroxyl radicals. The products of degradation with $K_2S_2O_8$ are yellowish in color and transparent. The subtracted IR spectra reveal a broad decrease of absorbance in the =C─H wagging at 835cm^{-1}, which indicate consumption of double bond during

degradation and no obvious changes in oxirane region of (Cis C-O) stretching vibration at 870 cm^{-1} (Figure 4.5) and the ratio of A_{835}/A_{2962} is shown in Table 4.3.

Figure 4.5: (a) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}) after 15 and 30 h reaction with $K_2S_2O_8$; (b) Changes in subtracted IR spectra in the 1000 -1150 cm^{-1} region.

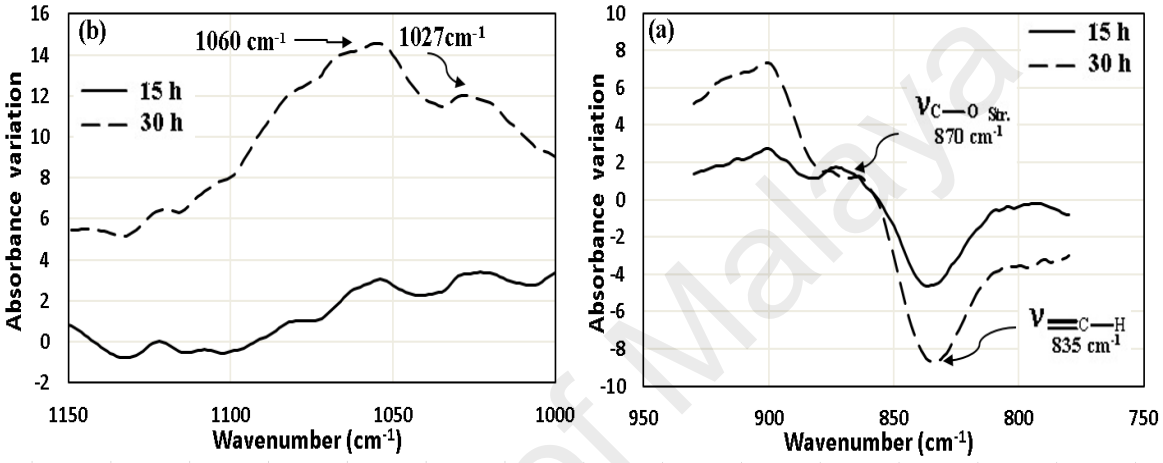


Table 4.3: Ratio of absorption of different functional groups to C-H stretching of methyl group after reaction with $K_2S_2O_8$.

Reaction time (h)	A835/A2962	A1060/A2962	A1027/A2962
0	0.9163	0.8288	0.8283
15	0.8884	0.8745	0.8802
30	0.8464	1.0346	1.0043

IR spectra of products indicate a growth of bands at 1027 cm^{-1} and 1060 cm^{-1} which could be related to C─OH stretching of alcohols (Figure 4.5 and Table 4.3). The small absorption band at 1735 cm^{-1} belonging to impurities of ENR25 (Chaikumpollert et al., 2011) shifted throughout the reaction to 1717 cm^{-1} which could assign to ketone. By proceeding of the reaction, a small shoulder appears at 1738 cm^{-1} and 1775 cm^{-1}. By

increasing the reaction time a great shoulder with the same intensity as bond at 1717cm^{-1}, appear at 1738 cm^{-1} Figure 4.6 and Table 4.4. The band at 1775 cm^{-1} can be related to lactone (Piton & Rivaton, 1996) . The broad band at 3438 cm^{-1} belonging to hydroxyl groups has significantly increased after 30 h as compared to that at 15 h of reaction (Figure 4.6 e and Table 4.4). Presumably during the prolonged reaction time, some carboxylic acid terminals could be generated, at the same time a small amount of epoxide groups have undergone hydrolysis to diols, whereby increasing the –OH content. Inevitably these some carboxylic acid group would react with the hydroxyl group to form ester, as noted and discussed in the NMR study in the next part.

Figure 4.6: (a) Changes in subtracted IR spectra in the carbonyl vibration region after 15 and 30 h reaction with $K_2S_2O_8$; (b) Changes in subtracted IR spectra in the hydroxyl vibration region.

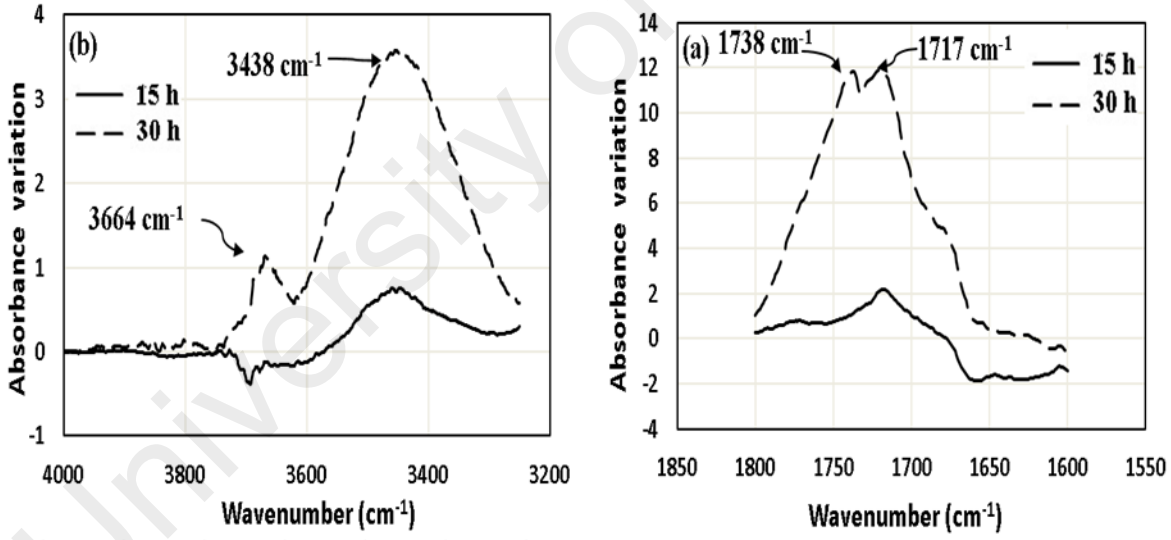


Table 4.4: Ratio of absorption of different carbonyl and hydroxyl groups to C-H stretching of methyl group after reaction with $K_2S_2O_8$.

Reaction time (h)	A_{1717}/A_{2962}	A_{1738}/A_{2962}	A_{1775}/A_{2962}	A_{3438}/A_{2962}	A_{3664}/A_{2962}
0	0.7610	0.7621	0.7539	0.7712	0.7542
15	0.7966	0.7890	0.7781	0.7954	0.7712
30	0.8456	0.8196	0.8023	0.8173	0.7790

^{1}H-NMR spectrum of the products reveal these new peaks in comparison with ENR25 (Figure 4 8): 2.34 ppm (s,C***H*****$_2$**COOCH3), 3.64 ppm (s,CH_2COOC***H*****$_3$**), 3.88 ppm (m, C***H*****─OH). The ^{1}H-NMR discloses also a very small peak at 9.78 ppm (s,CH_2C***H***O) and 9.5 ppm ,which can related respectively to aldehyde and α-β unsaturated aldehyde. The divided integration area of the signals at 5.1 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) shows a continuous decrease of double band (Figure 4.7). The molecular weight of the rubber after the reaction with potassium peroxodisulfate was reduced related on the reaction time. The molecular weight and the polydispersity index observed after degradation of ENR25 are present in Table 4.5.

Table 4.5: Results of average molecular weight and polydispersity index after reaction with $K_2S_2O_8$.

Reaction time (h)	M_n	M_w	PDI
0	148391	695508	4.68
15	11920	30376	2.54
30	4249	10476	2.46

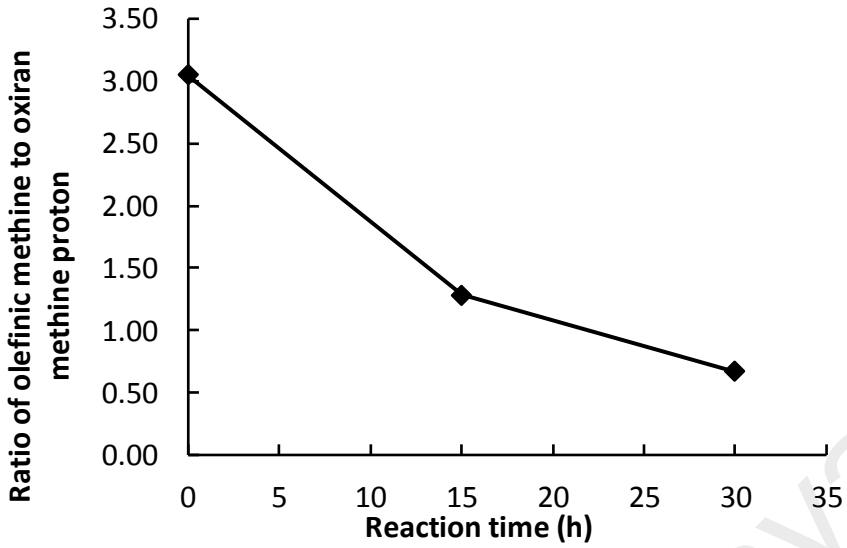


Figure 4.7: Ratio of integration area of the signals at 5.1ppm. (olefinic methine proton) and 2.7 ppm (epoxy methine proton). after reaction with $K_2S_2O_8$.

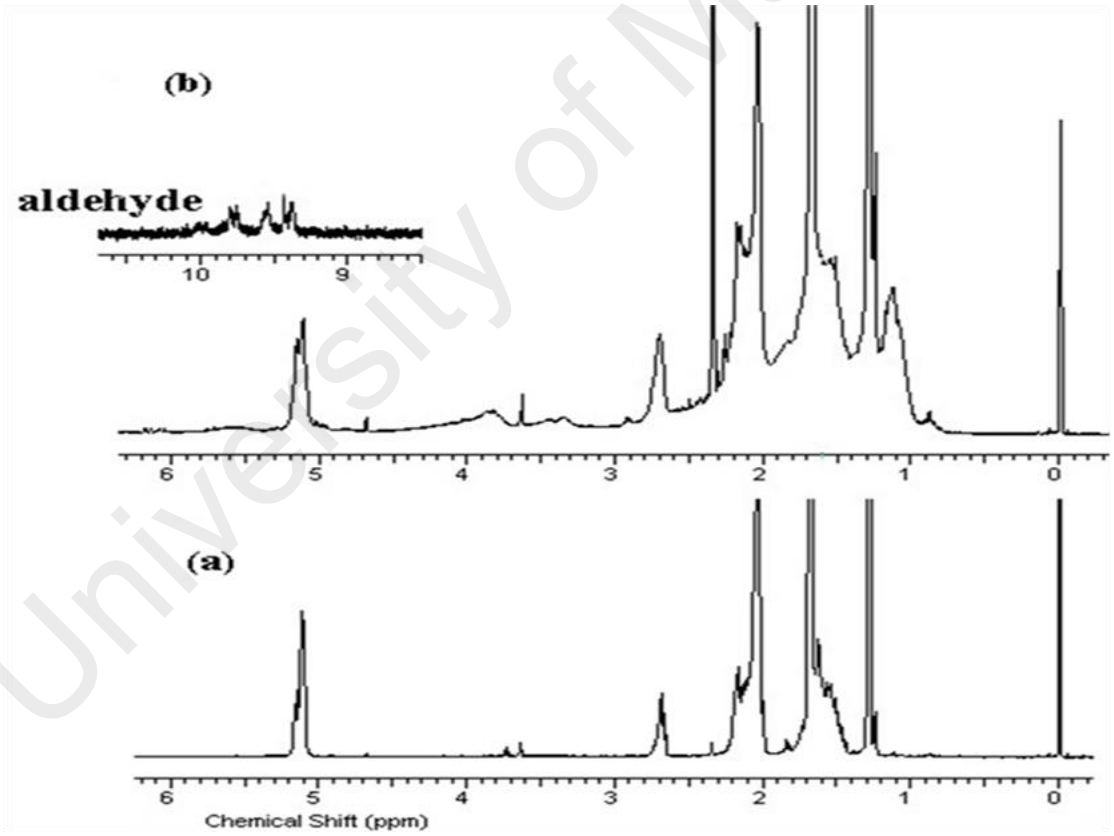


Figure 4.8: ^{1}H-NMR of (a) epoxidized natural rubber; (b) LENR after 30 h reaction with potassium peroxodisulfate

4.1.4 UV degradation method A

Degradation of epoxidized natural rubber has been described before but only a few papers have dealt with photo oxidation of rubbers in solution. The formation of cyclic and carbonyl product has been reported. During the UV irradiation, free radicals are formed (Dos Santos et al., 2005). These radicals attack double bonds to form unstable peroxy radicals in present of oxygen. The degraded rubber contains alcohol, ketone aldehyde and hydrogen peroxide groups (Adam et al., 1991). The liquid ENR obtained from UV degradation is clear and transparent. The subtracted IR spectra reveal that absorption band at 835 cm^{-1} (=C-H wagging) decreases continuously during the irradiation (Figure 4.9), which is consistent with the involvement of double bonds during the chain scission. Figure 4.9b shows the change in IR spectra in the ratio of A_{835}/A_{2962} at different duration of UV irradiation. The absorption peak at 2962 cm^{-1} belongs to C-H stretching of methyl group, which is not affected noticeably (Figure 4.2). The stretching vibration of oxirane ring at 870 cm^{-1} shows no substantial change in Figure 4.9a, which means that oxirane group was not involved in the chain scission reaction. The IR spectra reveal an increase of the absorption band at 1025 cm^{-1} (Figure 4.10) which stop increasing after 8 h irradiation. On the other hand, the absorption band at 1067 cm^{-1} rises continuously to get one of the most intense peak after 15 h irradiation. As photolysis proceeds a decrease of the absorption band at 1450 cm^{-1} (CH_2 deformation) could be observed and its adsorption intensity becomes less than the band at 1377 cm^{-1} which can relate to CH_3 asymmetric deformation. This perception could be related to consumption of methylene group during irradiation. In the carbonyl range the consequences of photolysis appear more complex.

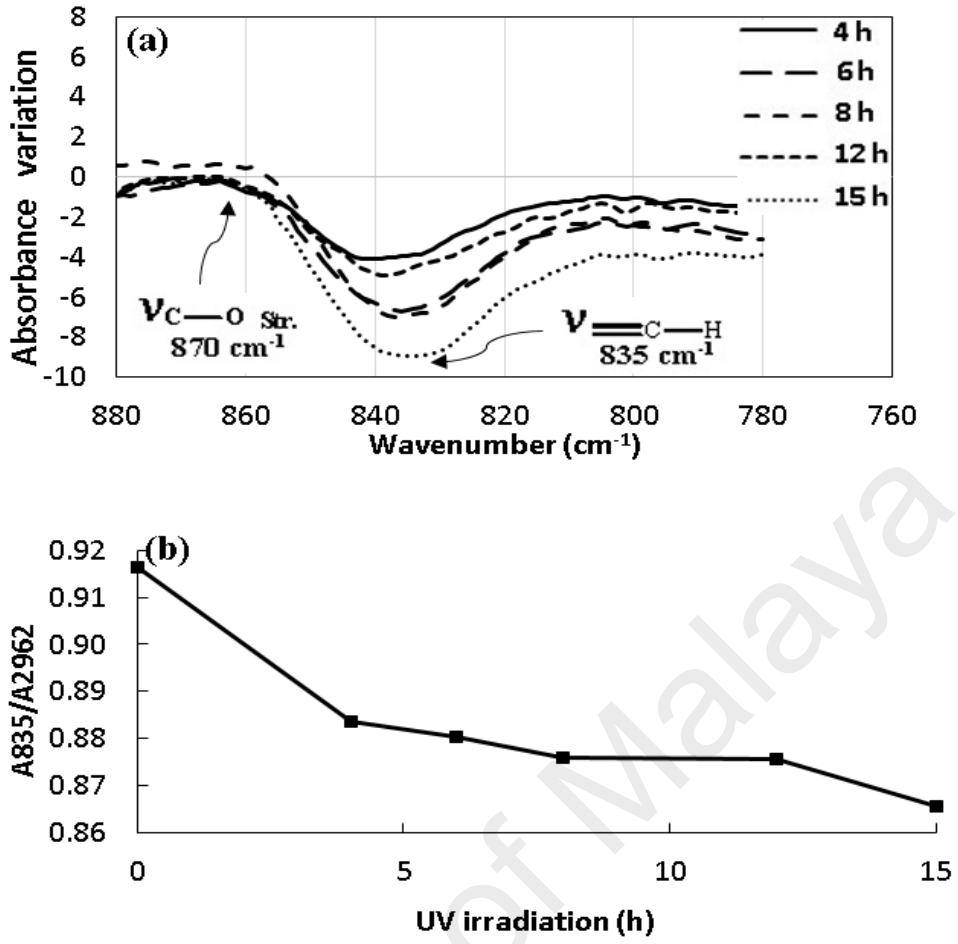


Figure 4.9: (a) Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}); (b) ratio of A_{835}/A_{2962} of degraded ENR during UV irradiation.

During the first 8 h of photo oxidation the band at 1717 cm^{-1} kept on increasing but thereafter two shoulders appears at 1736 cm^{-1} and 1775 cm^{-1} while there is a reduction in1717 cm^{-1} after 12 and 15 h of reaction (Figure 4.11). The maximum at 1717 cm^{-1} has been formerly assigned to methyl ketone (Adam et al., 1991). The hydroxyl region reveals a broad absorption band between 3300 cm^{-1} and 3600 cm^{-1} with a maximum at 3358 cm^{-1} which will be shifted during the reaction to 3438 cm^{-1} (Figure 4.12). The band at 3438cm^{-1} and 3358 cm^{-1} can be respectively assigned to associated alcohols and associated hydro peroxides (Adam et al., 1991).

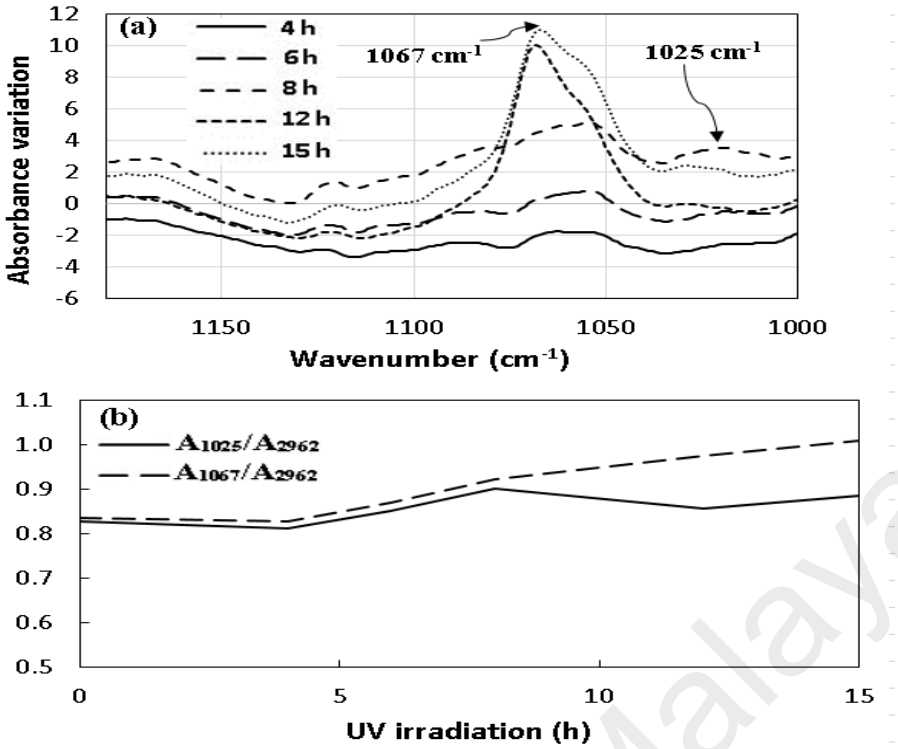


Figure 4.10: (a) Changes in subtracted IR spectra in the 1000 – 1150 cm^{-1} region; (b) ratio of absorption of different group to C-H stretching of methyl group at 2962 cm^{-1}.

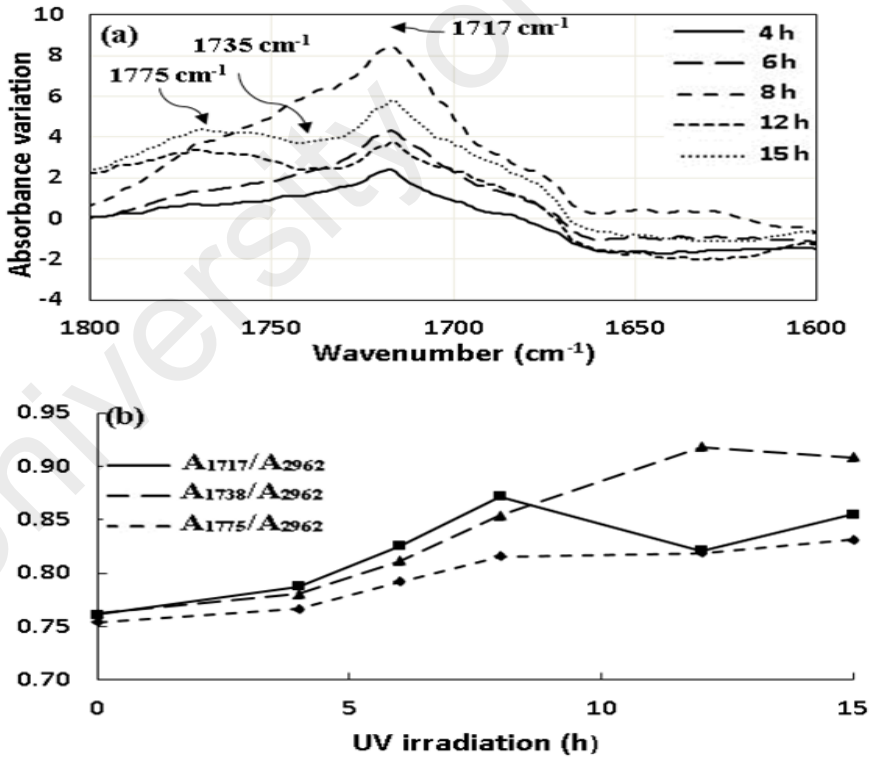


Figure 4.11: (a) Changes in subtracted IR spectra in the carbonyl vibration region; (b) ratio of absorption of different carbonyl group to C-H stretching of methyl group.

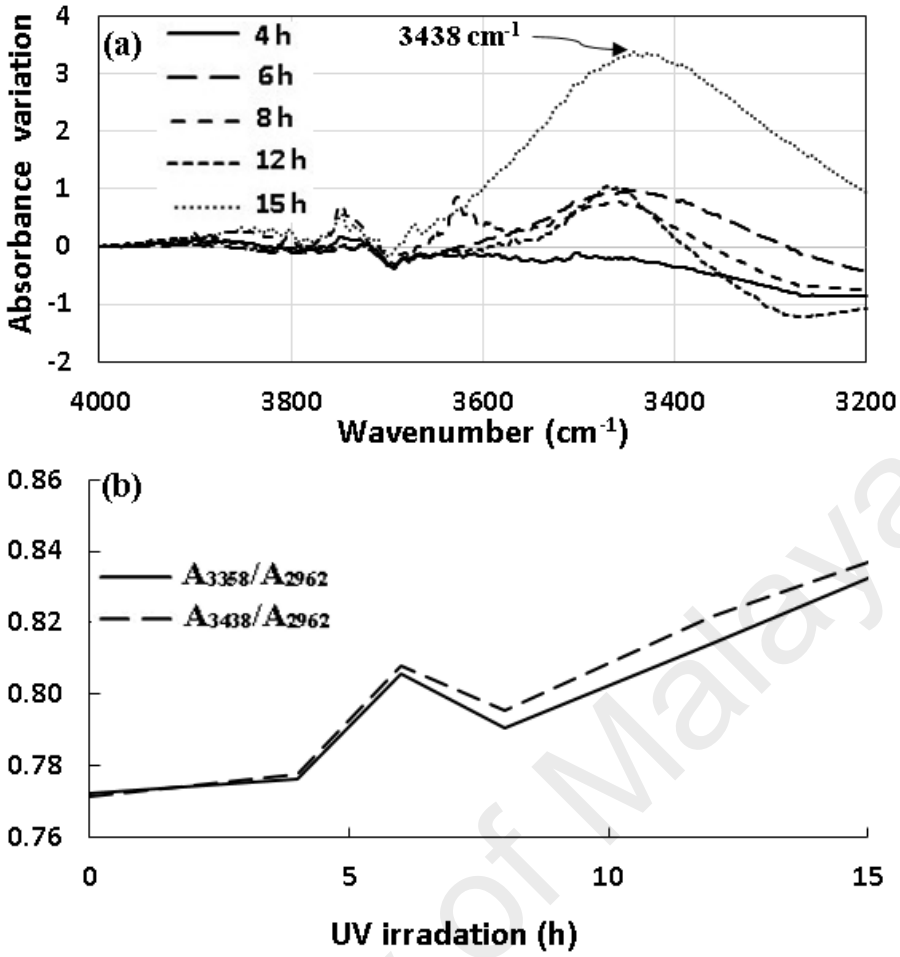
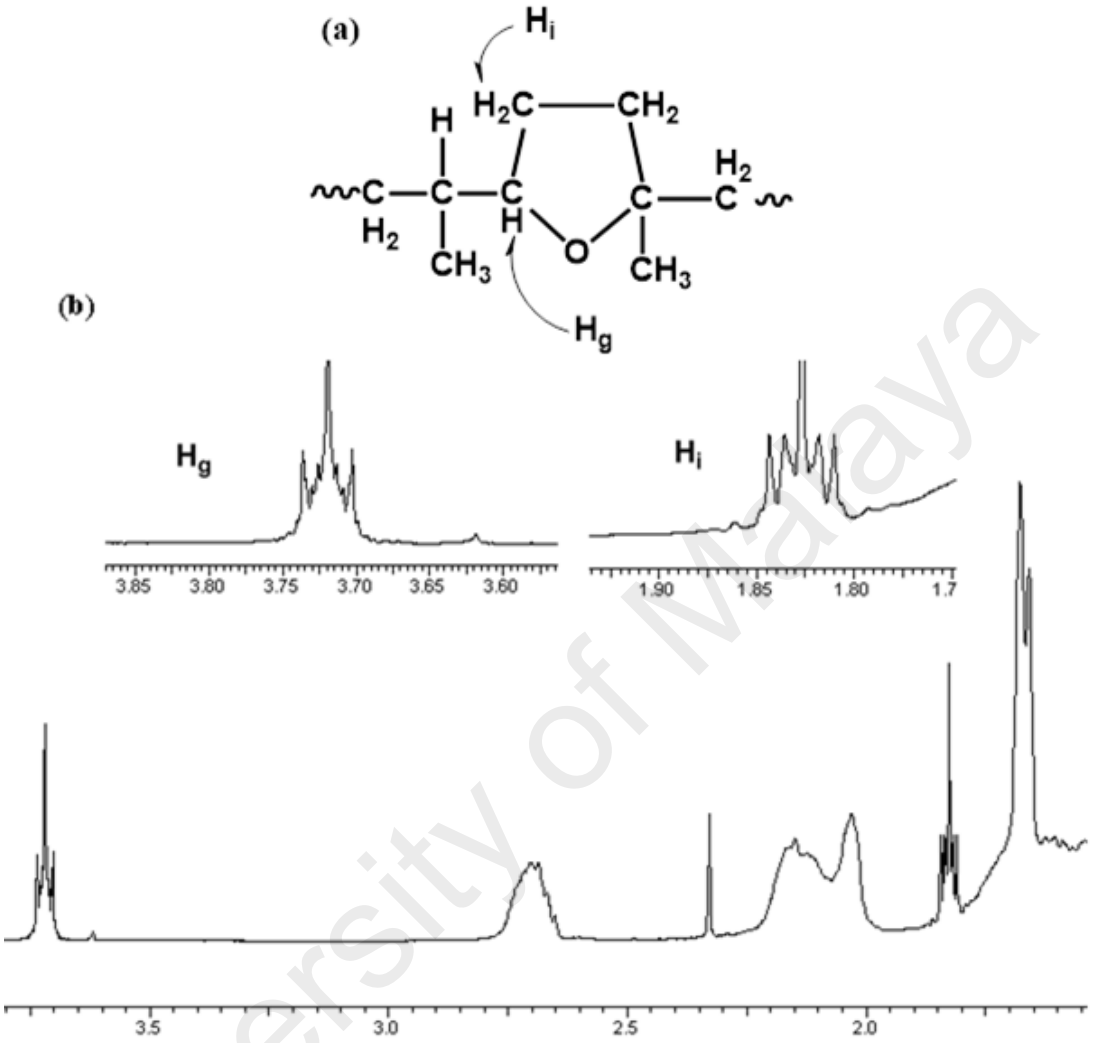


Figure 4.12: (a) Changes in subtracted IR spectra in the hydroxyl vibration. region; (b) the ratio of peaks at 3358 and 3438 cm^{-1} to C-H stretching of methyl group at 2962 cm^{-1} .

The ^{1}H–NMR spectra of degraded products reveal similar peaks with different intensities at various irradiation times ^{1}H–NMR δ (ppm): 1.29 ppm (s, C***H*****$_3$**COoxiraneCH), 1.67 ppm (s, ─C***H*****$_3$** isoprenic), 2.04 ppm (m, ─C***H*****$_2$** isoprenic), 2.34 ppm (s, C***H*****$_2$**COOCH$_3$), 2.7 ppm (t, CH$_3$COoxiraneC***H***─), 3.64 ppm (s,CH$_2$COOC***H*****$_3$**), 5.14 ppm (t,=C***H*** isoprenic). Also, a peak with small intensity was observed at 9.78 ppm (s, CH$_2$C***H***O) and 9.5 ppm, which can relate respectively to aldehyde and α-β unsaturated aldehyde. Furthermore, two other peaks appeared at 1.83 ppm (m) and 3.72 ppm (m) which could be related to the hydrofuranic structure (Figure 4.13) (Mistry, 2009). This is proven from the splitting pattern and chemical shift as shown in Figure

4.13 and Figure 4.14 (Zhang et al., 2010). The ratio of integration area of H_i to H_g in the



sample after 6 h irradiation is equal to 1.99.

Figure 4.13: (a) ^{1}H–NMR of hydrofuranic structure; (b) degraded ENR25 and splitting pattern of H_i (m, 1.83 ppm) and H_g (m, 3.73 ppm).

By dividing of integration area of the signals at 5.14 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) the variation of double bond concentration was investigated as shown in Figure 4.15. As Figure 4.15 shows, shows, a great reduction of double bond occurs at the first 4 h of UV degradation.

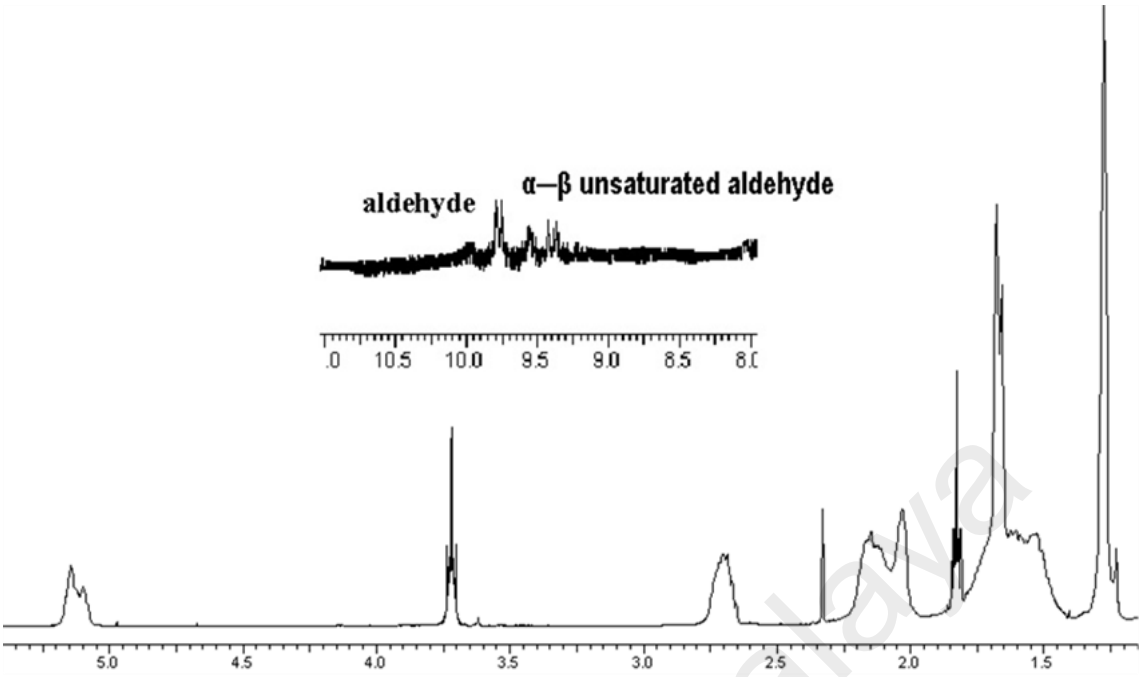


Figure 4.14: ^{1}H-NMR spectrum of degraded epoxidized natural rubber after 8 h UV irradiation.

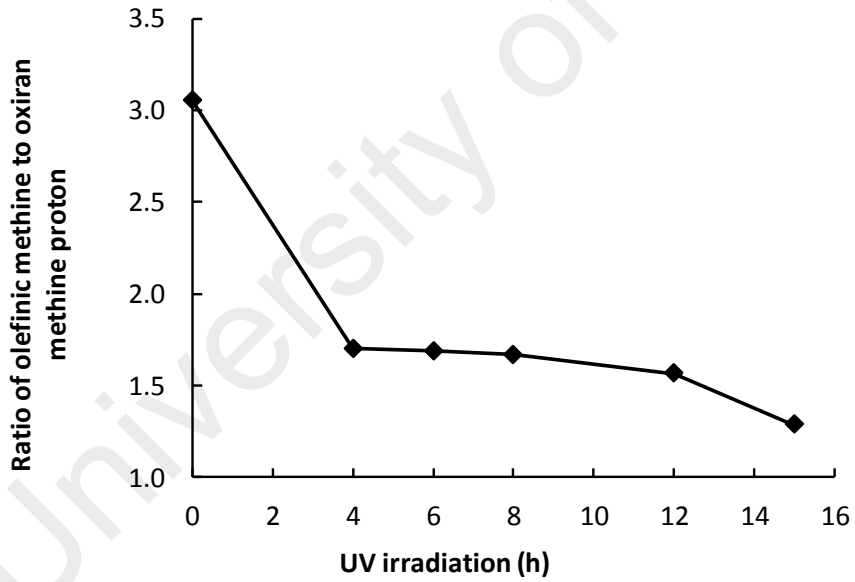


Figure 4.15: Decreasing of double bond intensity during photo oxidation calculated by comparing of integration area of the signals at 5.14 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton).

It was reported formerly that oxygen concentration should accelerate the degradation reaction (Dos Santos et al., 2005). A stream of air flow (55 ml/min) was induced deep inside the solution which was under UV radiation to see the effect of increased oxygen concentration on the products. The comparison of subtracted IR

spectrum in hydroxyl and double bond region of air blown sample with normal sample (without air flow) reveals that both samples follow similar pattern (Figure 4.16 – Figure 4.18). In the region of carbonyl vibration shown in Figure 4.17 the blown sample appears a peak with a maximum at 1738 cm^{-1} with a shoulder at 1717 cm^{-1} but the sample without air stream the maximum peak appeared at 1717cm^{-1} with a small shoulder at 1738 cm^{-1}.

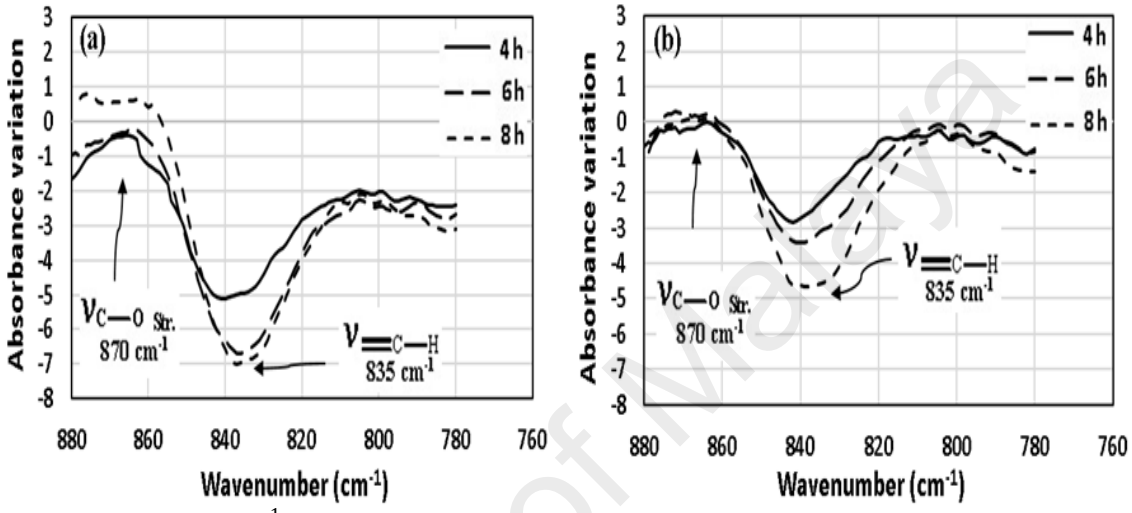


Figure 4.16: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in double bond region (=C-H 835 cm^{-1}) .

The change in molecular weight of ENR25 during photo oxidation was followed by GPC. Weight average molecular weight and polydispersity index decreased during the reaction time as is shown in Table 4.6. The molecular weight has a rapid decrease during the first four hour of the reaction. The M_n and M_w of air blown samples in all of three reaction time are unexpectedly greater than the relative unblown samples.

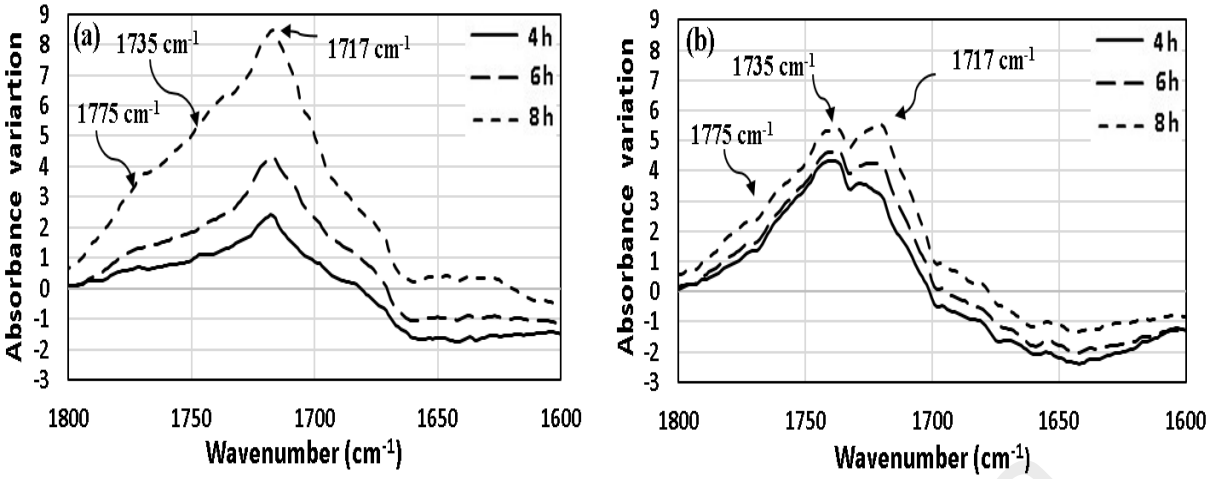


Figure 4.17: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in the carbonyl vibration region.

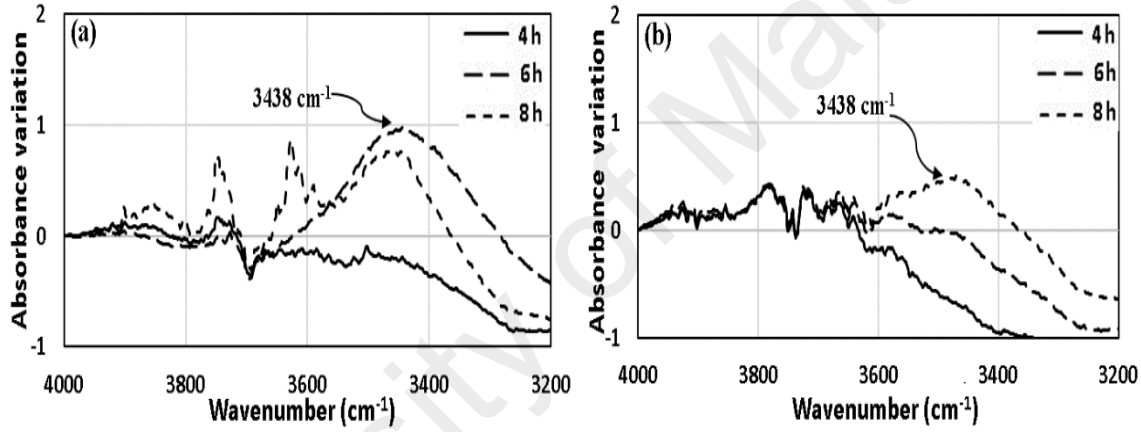


Figure 4.18: Changes in subtracted IR spectra during photo oxidation. Subtracted spectra between unblown sample (a) and air blown sample (b) in hydroxyl region.

Table 4.6: Results of average molecular weight and polydispersity indexafter UV irradiation.

Sample[a]	Reaction time (h)	M_n	M_w	PDI
A	0	148391	695508	4.68
A	4	14057	30080	2.13
A	6	11485	32533	2.83
A	8	9254	27698	2.99
A	12	9184	22177	2.41
A	15	7642	16953	2.21
B	4	18690	105127	5.62
B	6	13823	47273	3.41
B	8	11573	31516	2.72

[a] Sample A: Normal condition without air blowing; Sample B: Air blown.

4.1.5 Comparison of the three methods

To be able to compare these three methods together, degraded products of them with similar M_n where chosen and their subtracted IR spectra were investigated: 1- The irradiated ENR 25 after 6 h irradiation reached to M_n equal to 11485. 2- The ENR 25 after 15 h reaction with potassium peroxodisulfate gained a M_n of 11920.

3- The masticated ENR 25 after 8 h has a M_n of 11623.

The greatest decrease in the intensity of the double bond peak at 835 cm^{-1} belongs to the product of photo oxidation (Figure 4.19). In the same manner, the greatest increase in the intensity of peaks belonging to carbonyl and hydroxyl functional group can be seen by UV degradation product (Figure 4.20 and Figure 4.21).

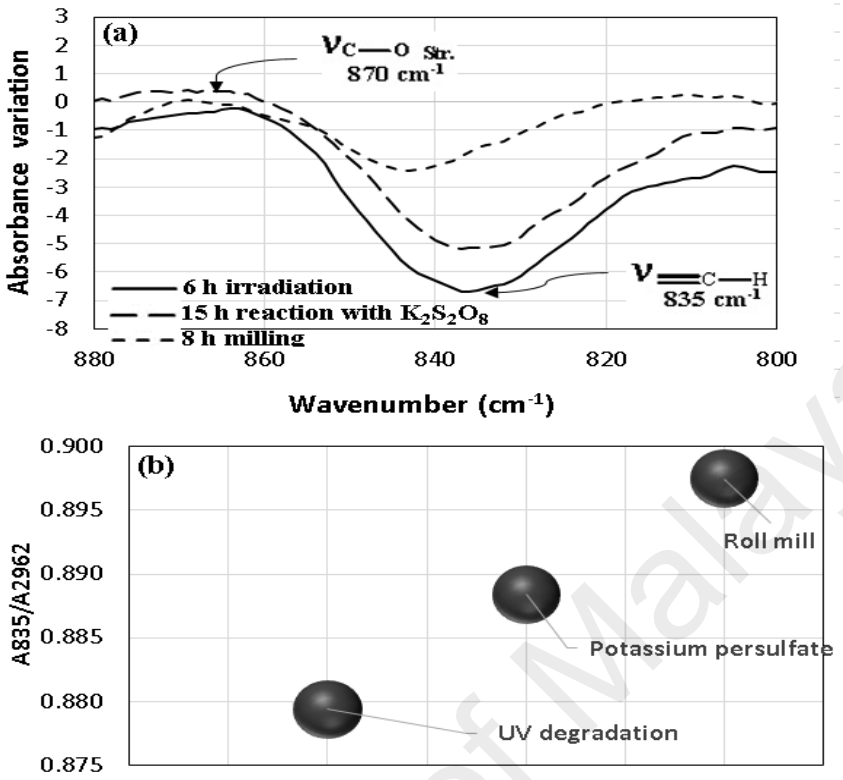


Figure 4.19: Changes in subtracted IR spectra in the double bond region (=C-H 835 cm^{-1}). A comparison of three degradation methods ; (b) ratio of A_{835}/A_{2962} of different degradation methods.

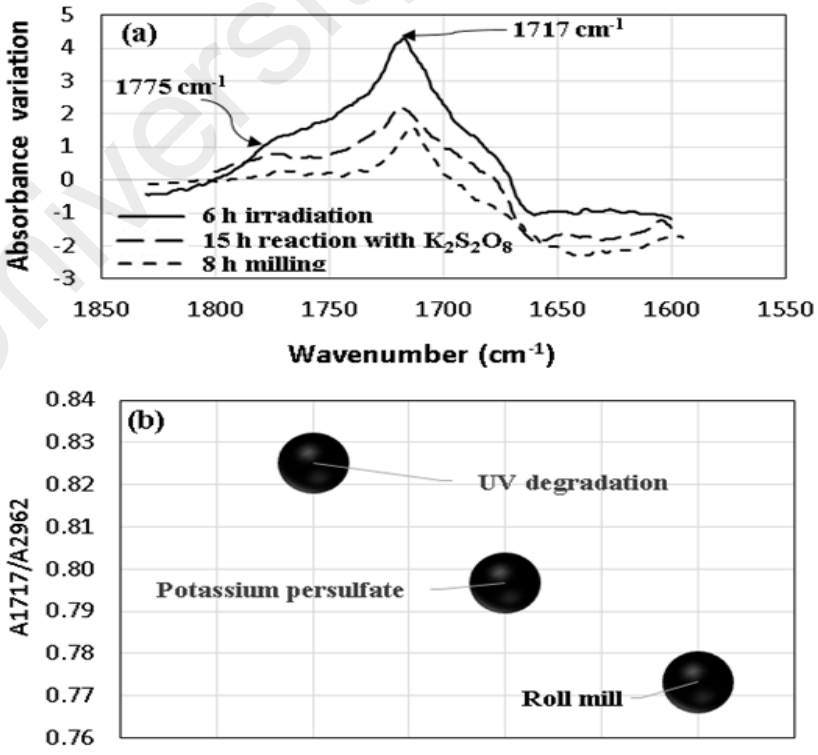


Figure 4.20: (a) Changes in subtracted IR spectra in the carbonyl vibration region. A comparison of three degradation methods; (b) ratio of A_{1717}/A_{2962} of different degradation methods.

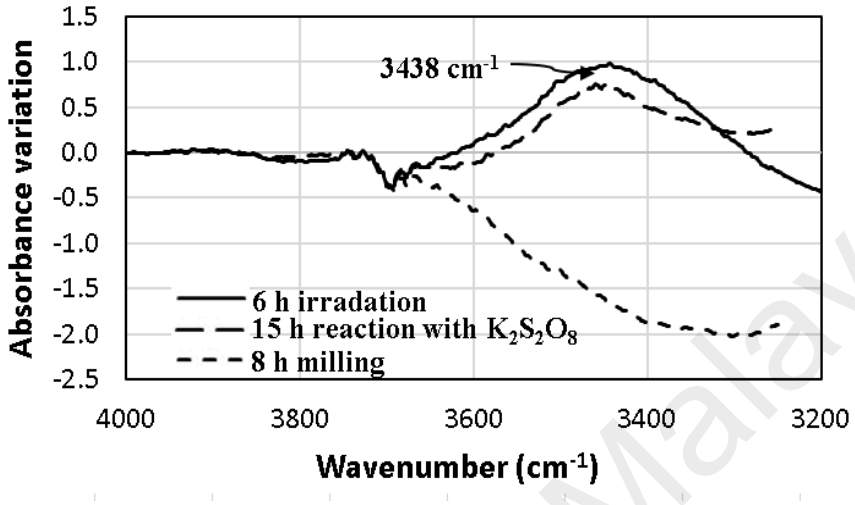


Figure 4.21: Changes in subtracted IR spectra in the hydroxyl region. A comparison of three degradation methods.

As mentioned before the epoxy content of degraded ENR was calculated by a method developed by Durbetaki (1956). Burfield & Gan (1975) showed that this method was applicable to ENR. The epoxy equivalent weight of degraded rubber indicated that there were no significant changes in epoxide content during degradation (Table 4.7).

Table 4.7: Results of epoxy equivalent weight of LENR obtained by different degradation methods.

Sample	epoxy equivalent weight (g/eq)	Percent of change
ENR	293	
LENR after 6 h irradiation	312	6.80%
LENR after 15 h reaction with K2S2O8	300	2.60%
LENR after 8 h milling	298	2%

All three methods in the present work degrade ENR 25 through radical mechanism. Chemical reactions which undergo through radical mechanism in polymeric material are complicated. In UV degradation, wavelength greater than 300 nm could not be absorbed by epoxidized natural rubber. Actually, impurities absorb the radiation to form radicals which initiated the reaction. Since radicals are generated they are able to abstract an allylic hydrogen or add to the double bond. Because numbers of double bond in photo oxidation and potassium peroxodisulfate reaction decrease dramatically the mechanism of addition to double bond is the main route. The created radical could react with oxygen readily if present, to produce peroxy radicals. In the absence of oxygen crosslinking reaction prevails. Peroxy radicals can abstract a hydrogen atom to convert to hydroperoxide. Hydroperoxide is not stable and could convert to alkoxy radical by loss of hydroxyl radical as is shown in Figure 4.22 (Adam et al., 1991).

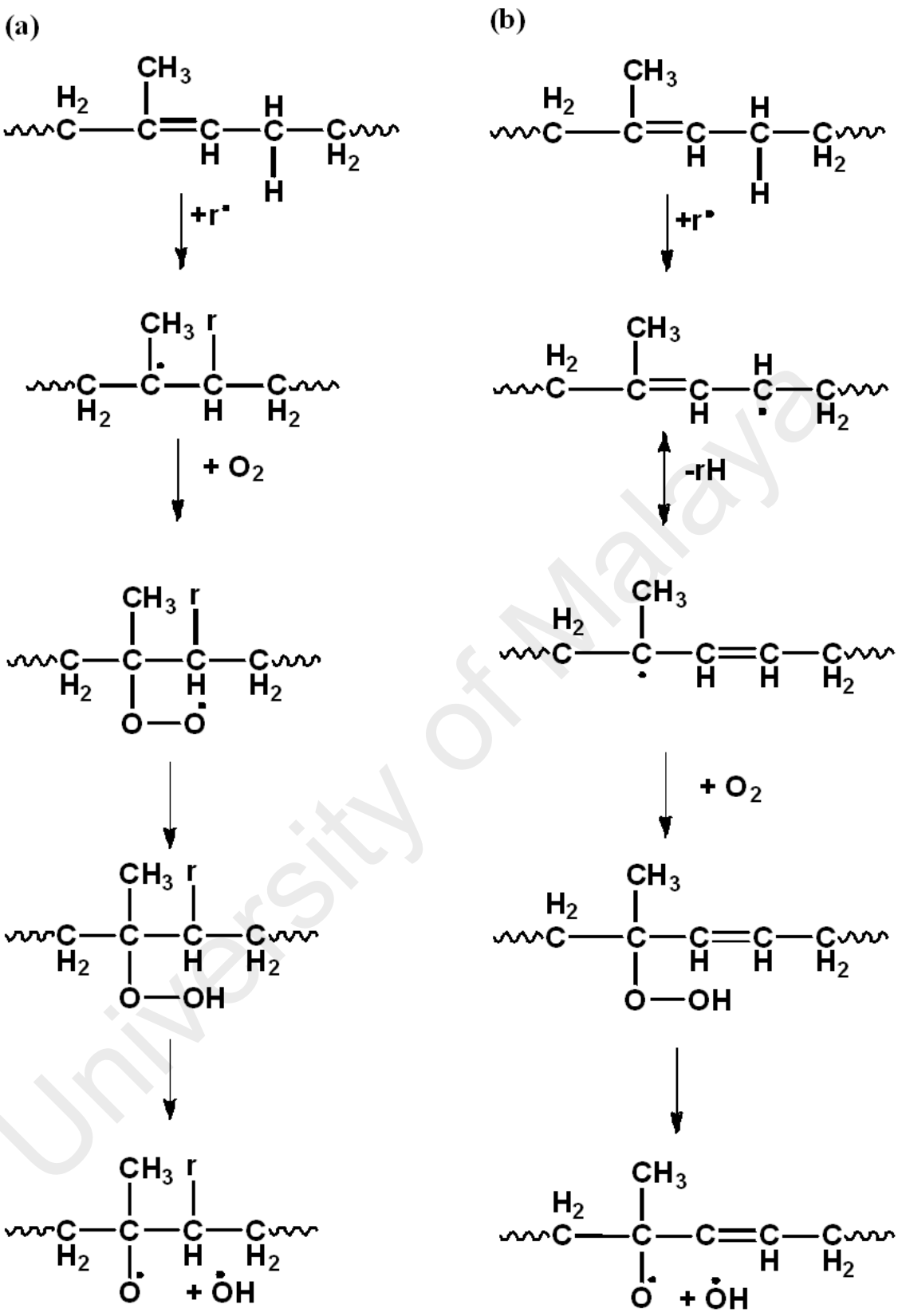


Figure 4.22: (a) Radical attack to the double bond of ENR 25. This is the main route in UV degradation and degradation with $K_2S_2O_8$; (b) Allylic hydrogen abstraction through radical attack.

The alkoxy radical formed can be transformed into alcohol or into different ketonic groups by β cleavage. By suggested mechanism through Claudie Adam et al. (Adam et al., 1991) after alkoxy radical is produced there will be a competition between converting to alcohol or doing β cleavage. Figure 4.23 shows radical attack directly to double bond which can generate alcohol and ketone. In the same manner alkoxy radicals produced by allylic hydrogen abstraction, can create unsaturated alcohol and ketone. A proposed plausible mechanism is shown in Figure 4.24.

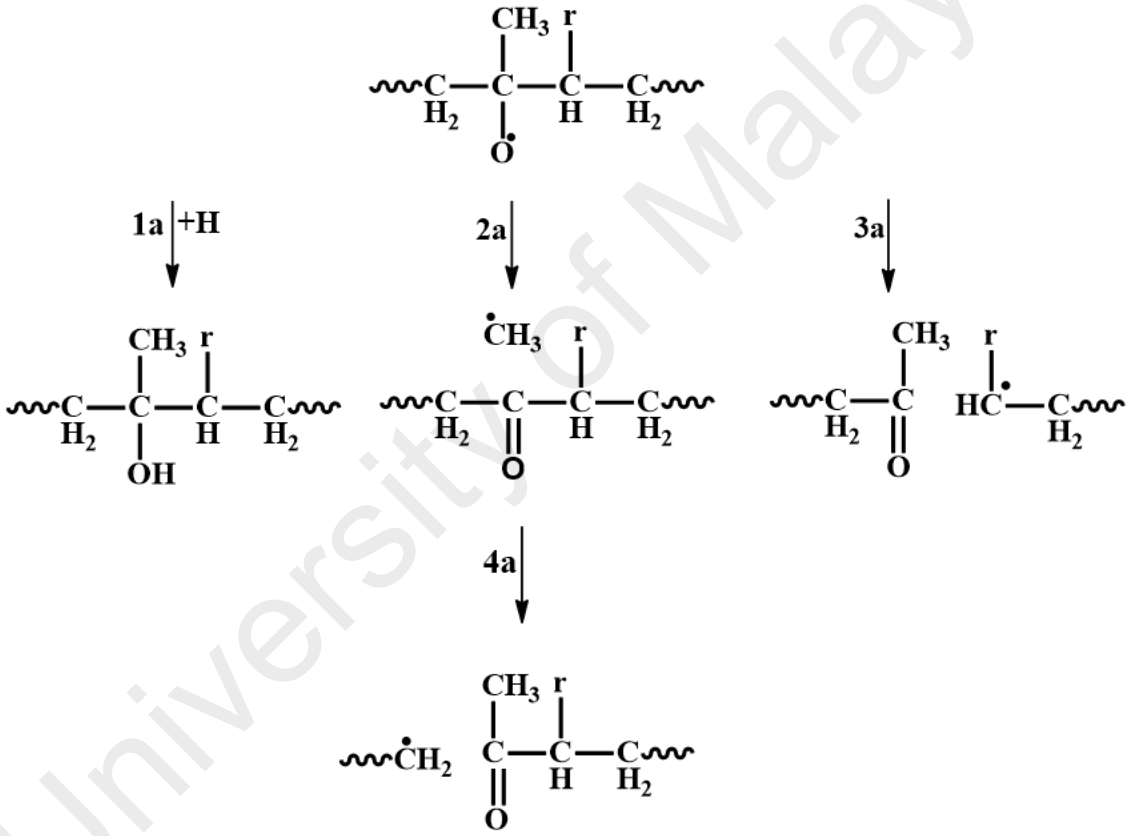


Figure 4.23: Free radical attacks double bond to produce alkoxy radical which can convert to alcohol (route 1a) or by β cleavage generate ketone (route 2a, 3a, 4a).

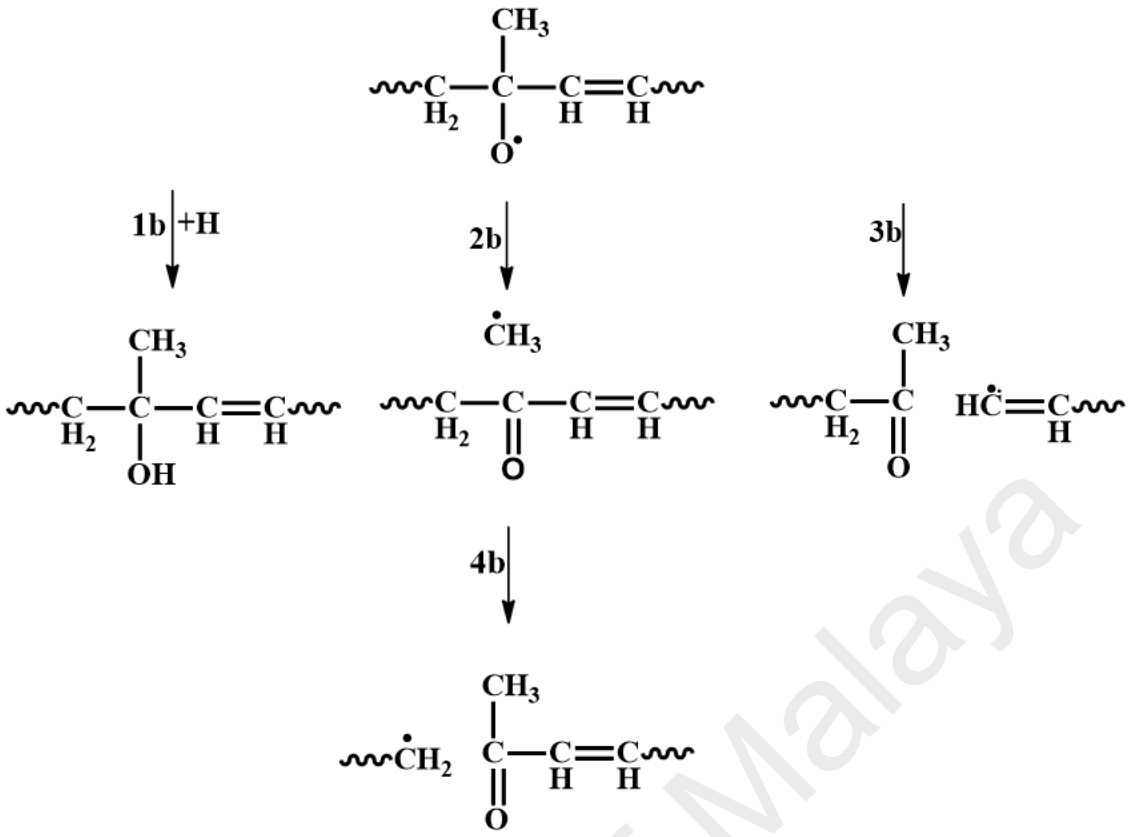


Figure 4.24: Free radical abstracts allylic hydrogen to produce alkoxy radical which can convert to alcohol (route 1b) or by β cleavages generate unsaturated ketone (route 2b, 3b, 4b) . The main routes are 1b and 4b.

The route 1a and 1b will result in alcohol and enol products. The paths 3a, 3b and 4a, 4b result in chain degradation and production of saturated and unsaturated ketones. The absorption band at 1717 cm^{-1} could be attributed to ketones and the absorption peak which appears at 1712 cm^{-1} in roll mill degraded product could be related to unsaturated ketones which could explain why in mastication there is no exact relation between chain scission and double bond deduction. Because by rupturing of primary bond between the neighboring methylene groups, two allyl radicals will be generated (Pike & Watson, 1952) (Figure 4.25) which could attack a double bond or convert to a more stable tertiary alkyl radical that can react with oxygen to produce peroxy radicals. This radical can convert to unsaturated ketone by β cleavage.

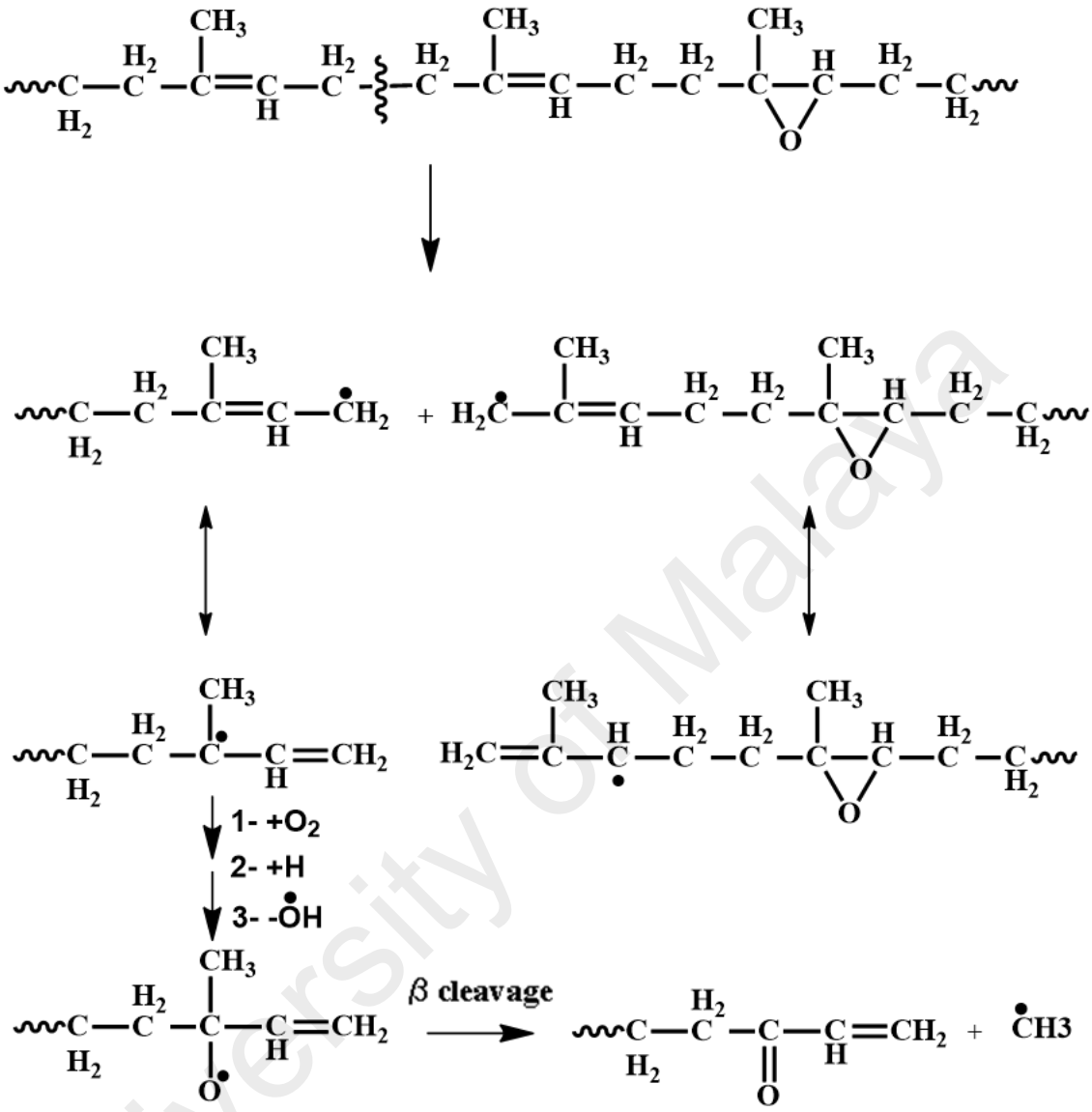


Figure 4.25: The weakest bond will be ruptured by applied force.during mastication and generate methylene radicals which ultimately produce unsaturated ketone.

In UV degradation method, hydrofuranic structure is one of the major products as ^{1}H–NMR reveals. It is worthy to mention that this structure could not be seen by the other methods. Figure 4.26 shows a suggested mechanism which cause hydrofuranic structure from alkoxy radicals.

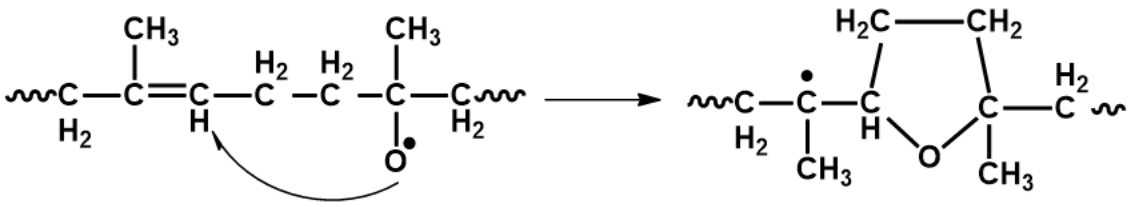


Figure 4.26: Proposed plausible mechanism to form hydrofuranic structure.from alkoxy radicals.

By continuation of UV degradation reaction as is shown in Figure 4.11 absorption peak at 1717 cm^{-1} decreased after 8-hour exposure and a broad shoulder at 1735 cm^{-1} and1775 cm^{-1} was formed. This phenomena could be explained by Norrish Ⅰ reaction (Laue & Plagens, 2005) (Figure 4-27). By this type of reaction, a bond between carbonyl group and an α-carbon is cleaved homolytically. The resulting radical can further react with alkoxy radicals due to an intermolecular reaction or intramolecular reaction which cause respectively lactone or ester shown in Figure 4.28 and Figure 4.29. The mentioned lactone has an absorption peak between 1775 cm^{-1} to 1780 cm^{-1}.

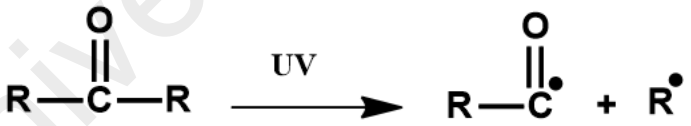


Figure 4.27: Nourish Ⅰ reaction .

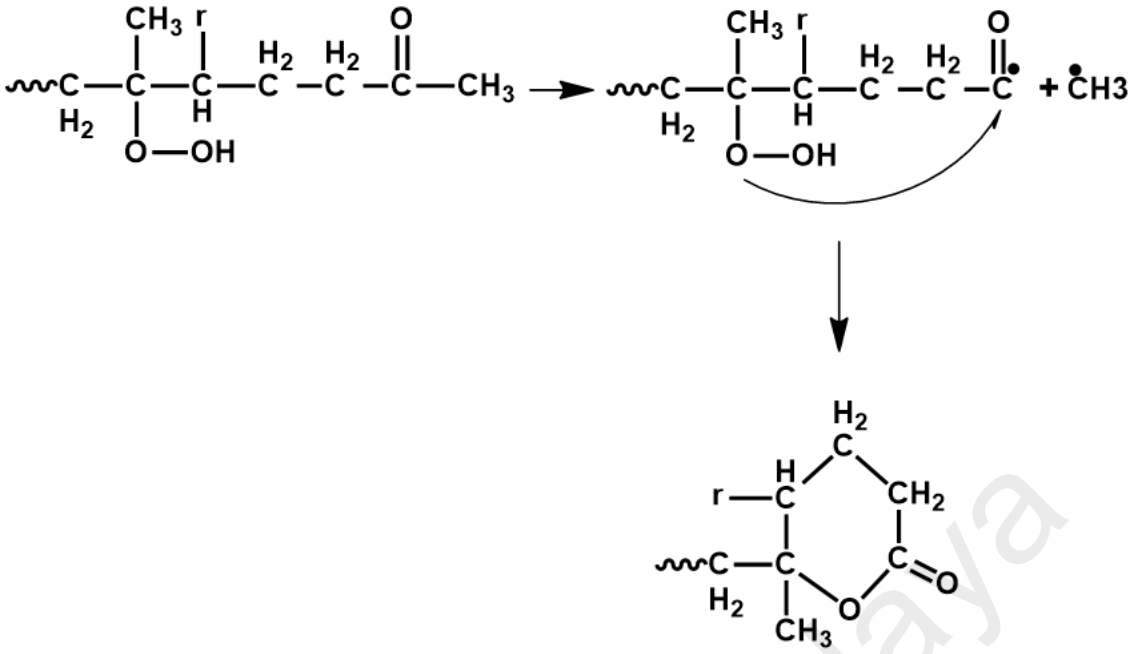


Figure 4.28: Intramolecular reaction of acyl radicals generated by Nourish I reaction with alkoxy radical adjacent to carbonyl group to produce lactone.

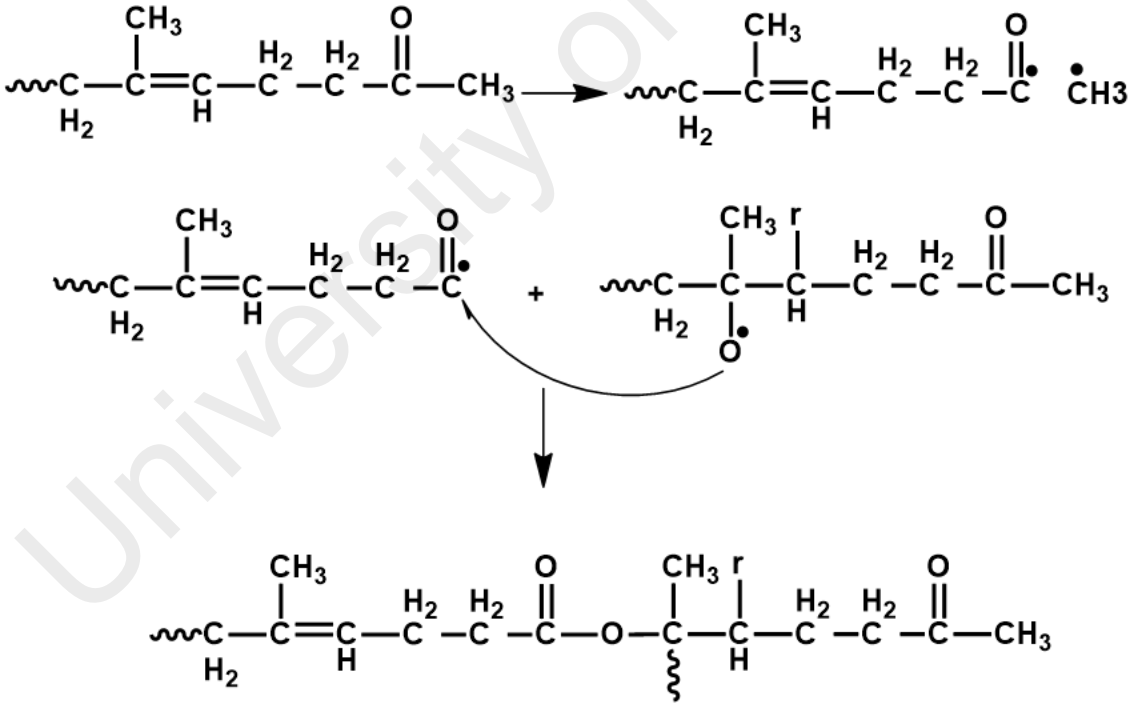


Figure 4.29: Intermolecular reaction of acyl radicals to form ester generated by Nourish I reaction with alkoxy radical of another molecule.

In all of three methods a small amount of aldehyde is generated; when peroxy radical attacks the nearest double bond aldehyde will be formed. Morand (1977) suggested a mechanism for aldehyde formation which is shown in Figure 4.30.

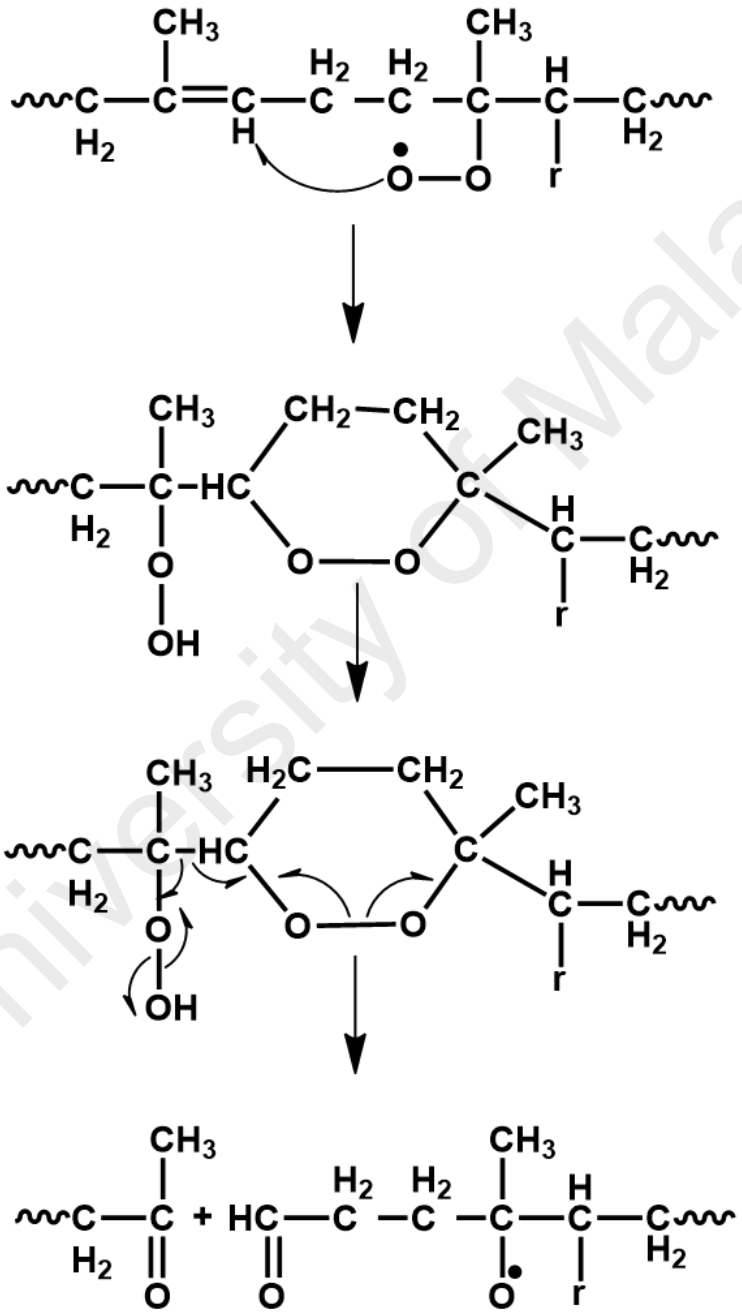


Figure 4.30: A plausible mechanism for aldehyde generation.

4.2 Preparation of LENR by oxidative degradation methods using H_5IO_6 and $KMnO_4$ and comparing them with UV degradation

4.2.1 Introduction

LENR could be prepared by different methods through cleavages of C=C or epoxide groups, or a combination of both sites. Different mechanisms would produce different terminals on the LENR. This chapter reports the oxidative degradation by (i) periodic acid, (ii) potassium permanganate and compared them with ultra violet (UV) irradiation. The UV degradation was done by increasing the intensity of UV radiation and using a thinner solution of ENR in toluene, because formerly it was reported that decreasing of the concentration would increase the efficiency of degradation in thinner solution (Ravindran et al., 1988). To observe the possible effect of oxirane group on degradation mechanism, NR is degraded in the same way as ENR.

4.2.2 Degradation by periodic acid

Periodic acid is an effective scission agent for glycol as reported by Malaprade (1928). The application of periodic acid to cleave oxirane group was reported by Eastham & Latremouille (1950). However, potassium periodate and other periodate salts could not cleave easily the epoxides but they could readily break the glycol bond. Marker et al. suggested that cleavage reaction of periodic acid begins with an acid catalyzed ring opening which goes further by nucleophilic periodate anion attack (Maerker & Haeberer, 1966). THF solutions of ENR 25 and NR were reacted separately with periodic acid in four different concentrations (0.026, 0.044, 0.075 and 0.145 mphr). After removing the solvent, the sticky products were yellowish and transparent. The subtraction of the initial FTIR spectrum of the undegraded from the degraded rubber,

allows the observation of several differences in the reactions. Double bond absorbance (=C-H 835 cm^{-1}) in Figure 4.31 reveals a decrease in band 835 cm^{-1} which indicates the reduction of double bond during degradation, and higher concentration of H_5IO_6 causes a greater decrease in the band. The oxirane stretching vibration (cis C-O) at 870 cm^{-1} has decreased with increasing H_5IO_6 concentration. Figure 4.31b shows the decrease in the ratio of A_{870}/A_{2962} for ENR25 being degraded using different concentrations of H_5IO_6. The C-H symmetrical stretching vibration band at 2962 cm^{-1} belonging to methyl group is not affected noticeably during the degradation as was observed in other methods described before (Figure 4.32). Degradation of NR with 0.075 mphr was carried out under the same conditions as ENR reaction. The subtracted IR spectra is shown in (e) in Figure 4.31, which reveals a significant decrease in double bond absorbance.

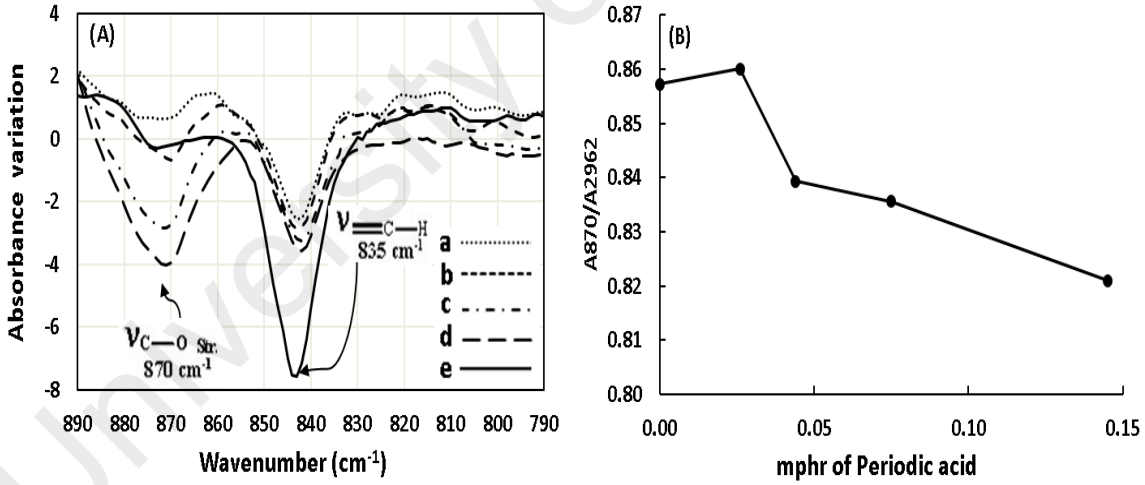


Figure 4.31: (A) Changes in absorbance of the double bond region (=C-H wagging) after 10 h reaction with various amounts of H_5IO_6: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{870}/A_{2962} of ENR degraded at different concentrations of H_5IO_6.

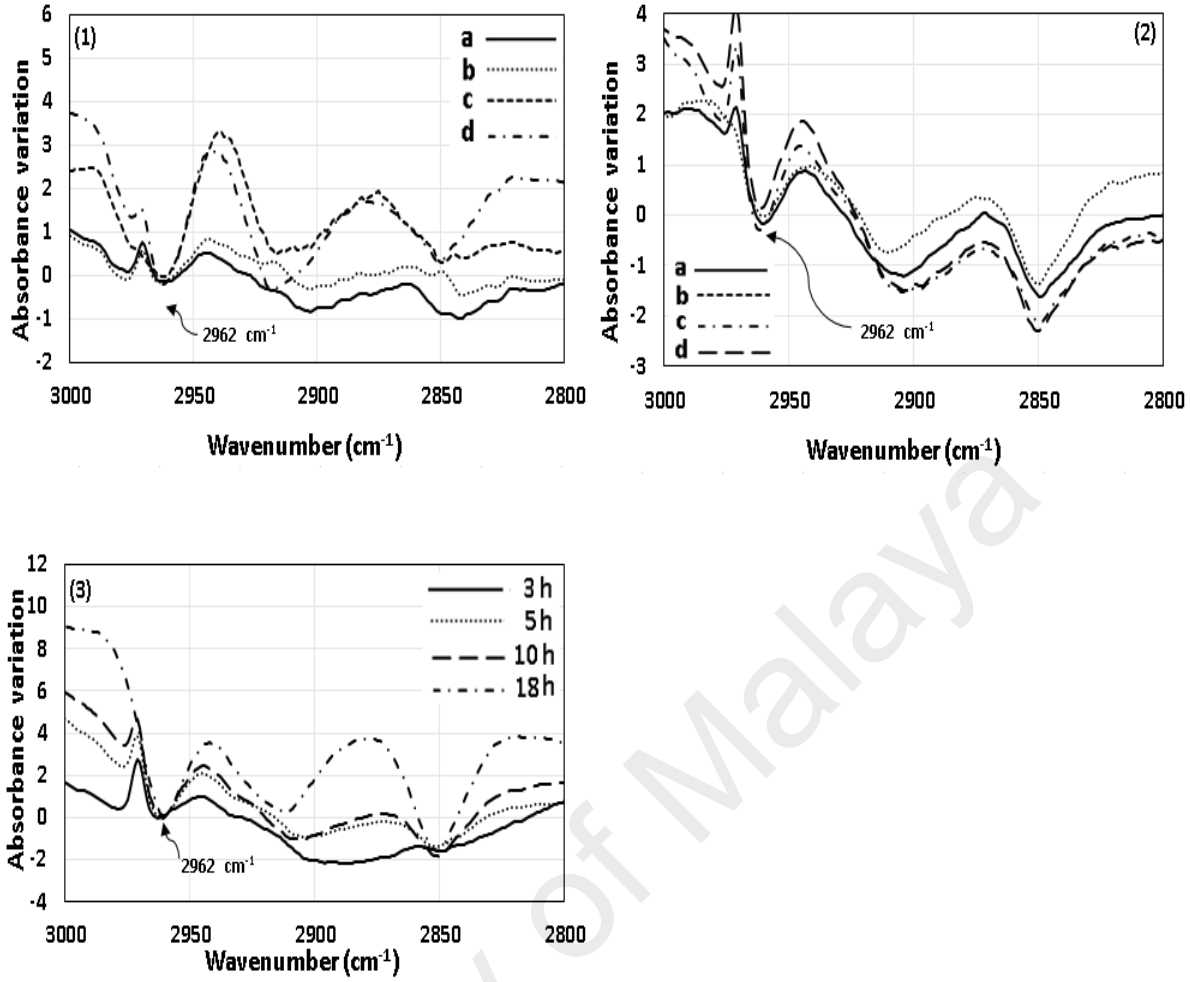


Figure 4.32: Changes in subtracted IR spectra in the region of 2962 cm^{-1} for different degradation methods: (1) Degradation with H_5IO_6; a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; and d, 0.145 mphr. (2) Degradation with $KMnO_4$; a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; and d, 0.145 mphr. (3) Degradation with UV after different irradiation times.

The use of a small amount of H_5IO_6 for degradation of ENR shows a rise in the band 1717 cm^{-1} and 1735 cm^{-1} which could be assigned to ketone and ester as shown in Figure 4.33 (Chaikumpollert et al., 2011). By increasing the amount of H_5IO_6 the peak at 1717 cm^{-1} becomes the most intense peak with a small shoulder at 1735 cm^{-1}. The absorbance peak of –OH moiety at 3452 cm^{-1} shows a decrease at lower concentration of H_5IO_6 but increases at higher concentration of reagent as is shown in Figure 4.34.

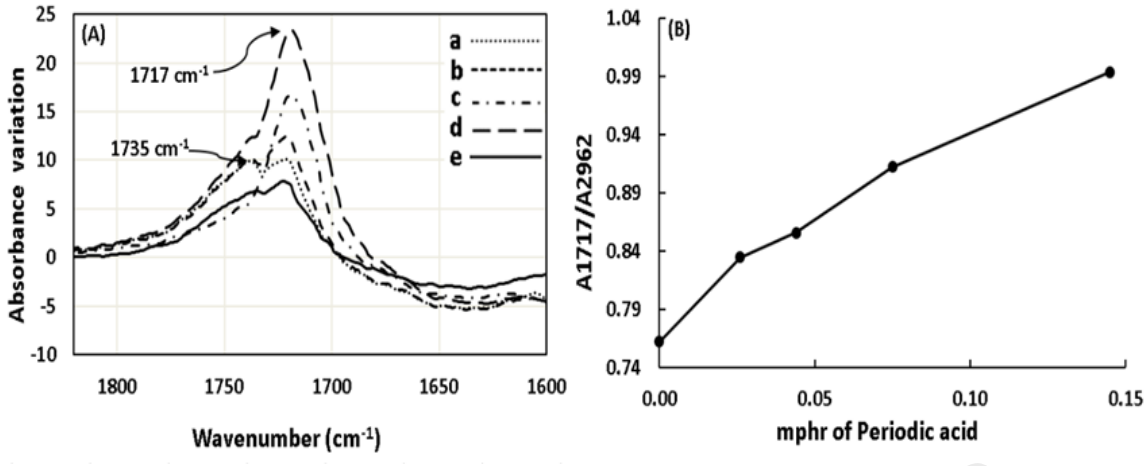


Figure 4.33: (A) Changes in absorbance of the carbonyl group after 10 h reaction with various amounts of H_5IO_6 :a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{1717}/A_{2962} of the degraded ENR with different amounts of H_5IO_6.

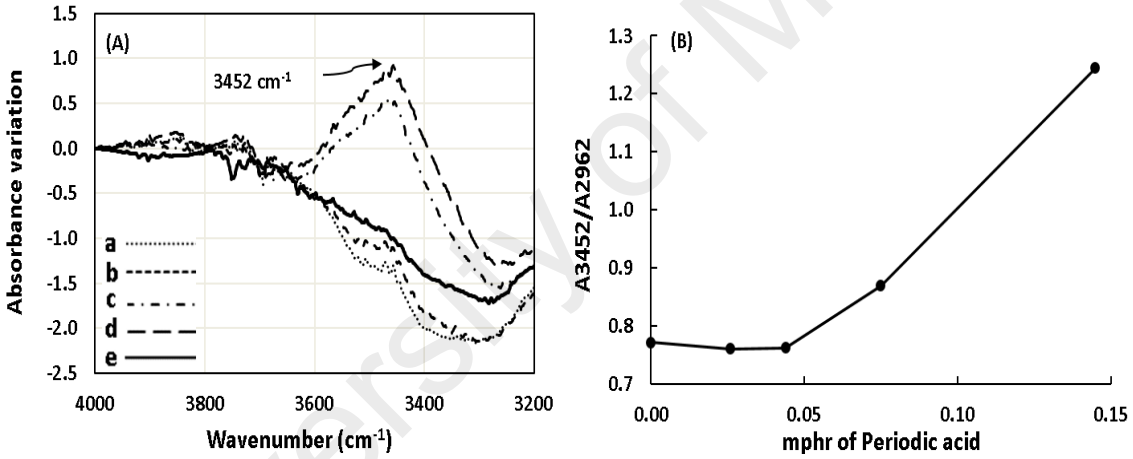


Figure 4.34: (A) Changes in absorbance of the hydroxyl group after 10 h reaction with various amount of H_5IO_6:a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr H_5IO_6. (B) Ratio of A_{3452}/A_{2962} of the degraded ENR with different amounts of H_5IO_6.

The ^{1}H-NMR spectra of the degradation products revealed similar peaks with different intensities at various concentration of H_5IO_6 as shown in Figure 4.35: 1.24ppm (C***H*****$_3$**CHOH), 1.29 ppm (C***H*****$_3$**COoxiraneCH-), 1.67 ppm (-C***H*****$_3$**isoprenic), 2.02 ppm (C***H*****$_2$**isoprenic), 2.24 ppm (CH_3COCH_2C***H*****$_2$**-), 2.34 ppm (C***H*****$_2$**$COOCH_3$), 2.44 ppm (CH_2C***H*****$_2$**CHO), 3.34 ppm (C***H*****$_2$**OH), 3.64 ppm (CH_2COOC***H*****$_3$**), 3.92 ppm (C***H***OH),

5.10 ppm (=C***H***isoprenic) 9.78 ppm (CH_2C***H***O) and a peak appears at 9.43 ppm which could be assigned to α-β unsaturated aldehyde. A small peak appears at 5.32 ppm which could be assigned to $=CH_2$ of cyclized isoprene unit. Under acidic conditions isoprene unit could undergo intermolecular cyclization which is accompanied by a partial loss of the original unsaturation (Sakdapipanich et al., 2002).

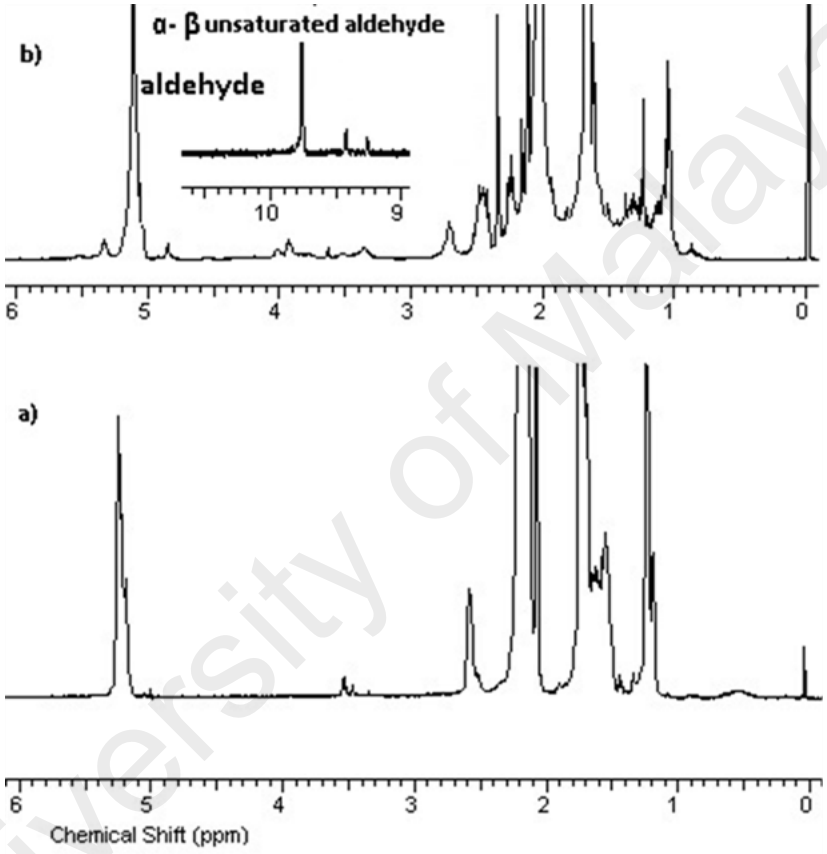


Figure 4.35: ^{1}H-NMR of (a) epoxidized natural rubber and (b) degraded ENR after reaction with 0.075 mphr H_5IO_6.

Figure 4.36 shows the ratio of integration areas of the signals at 5.1 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) of ENR 25 degraded with 0.026, 0.044, 0.075 and 0.145 mphr of H_5IO_6. At 0.026 mphr of H_5IO_6, the ratio has decreased, and subsequently increased at higher H_5IO_6, presumably the epoxide groups were reduced. To explain the initial decrease in the ratio, the epoxy content

needs to be determined, and this would be discussed later with reference to the data in Table 4.12.

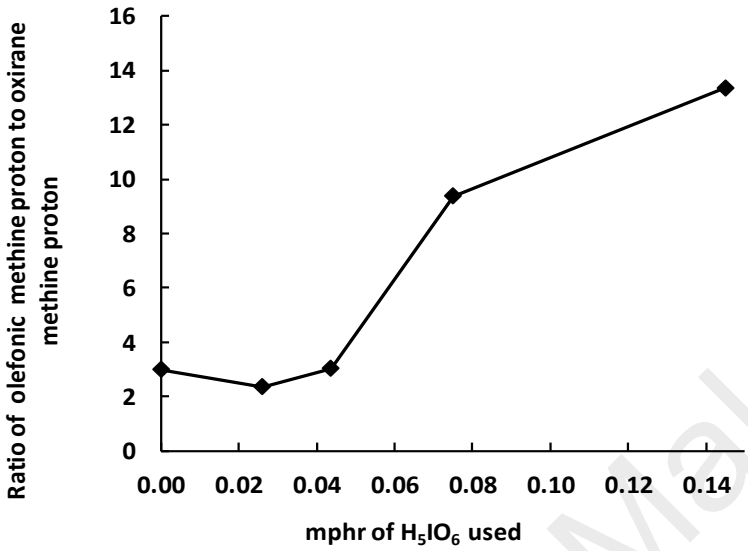


Figure 4.36: The ratio of the integration area of the signal at 5.11ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after degradation with different amounts of H_5IO_6.

The molecular weight of ENR has declined rapidly with increase H5IO6 concentration (Table 4.8) but there is no observable trend in polydispersity presumably due to more than one degradation mechanisms.

Table 4.8: Results of average molecular weight and polydispersity during degradation with H_5IO_6 after 10 h of reaction.

Amount of H_5IO_6 (mphr)	M_n	M_w	PDI
0	148391	695508	4.68
0.026	7307	31392	4.23
0.044	3907	9770	2.5
0.075	1281	5919	4.6
0.145	1269	3804	2.99

4.2.3 Degradation using potassium permanganate

Degradation of ENR by potassium permanganate has not been reported before. Oxidative cleavage of double bond with $KMnO_4$ is a very complicating reaction. The reaction of unsaturated hydrocarbons with $KMnO_4$ at room temperature under alkaline conditions yields cis diols (Wiberg & Saegebarth, 1957). $KMnO_4$ is a strong oxidizing agent which could oxidize the product further. Under acidic conditions, the cleavage of double bond occurs without formation of diol. The first step of reaction is followed by generation of cyclic manganate esters which undergo cyclic fragmentation (Dash et al., 2009). Manganese dioxide is produced during the reaction and the reaction mixture turns dark brown. The manganese dioxide is insoluble in THF and could be removed by filtration. Figure 4.37 shows the subtracted IR spectra of degradation products. The band at 835 cm^{-1} (=CH wagging) which indicate consumption of the double bond decreases with increasing the concentration of $KMnO_4$. A decline of band 870 cm^{-1}, attributed to oxirane group, is also observed. The ratio of A_{835}/A_{2962} is shown in Figure **4.37** (B). The subtracted IR of degraded NR which is shown in (e) in Figure 4.37 (A) reveals an intense decrease at the band 835 cm^{-1} (=CH wagging). Figure 4.38 shows band at 1717 cm^{-1} increases with the concentration of $KMnO_4$. The peak at 1735 cm^{-1} appears when $KMnO_4$ concentration is at 0.044 mphr and higher. This is assigned to the ester groups. This peak is not seen in NR.

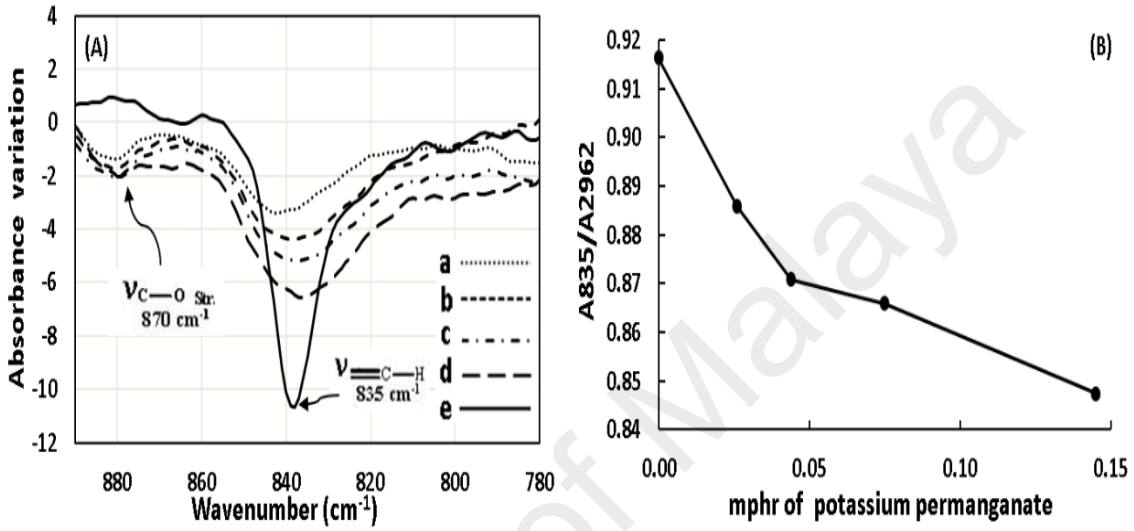


Figure 4.37: (A) Changes in absorbance of the double bond region (=C-H wagging) after 10 h reaction with various amounts of $KMnO_4$: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr $KMnO_4$. (B) Ratio of A_{835}/A_{2962} of ENR degraded at different concentrations of $KMnO_4$.

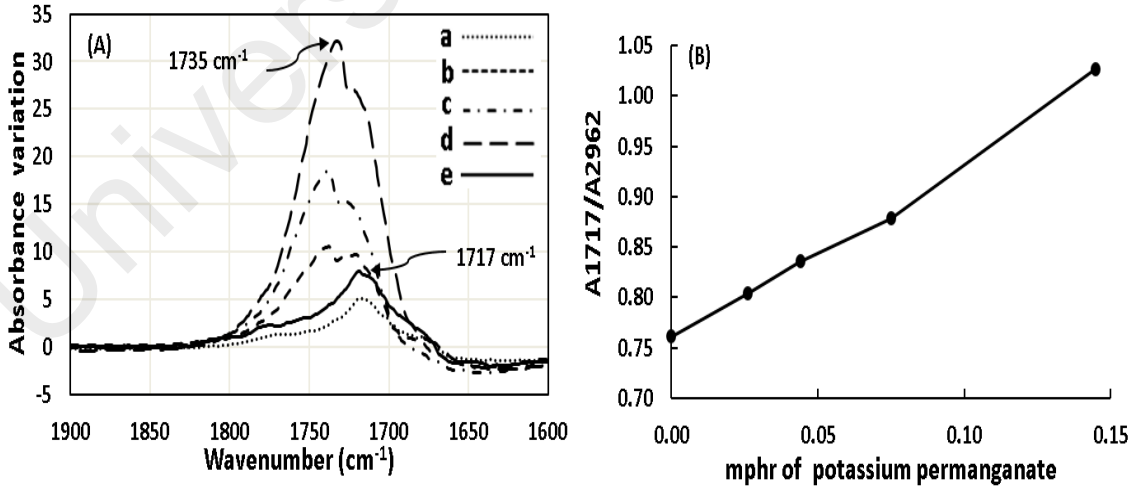


Figure 4.38: (A) Changes in absorbance of the carboxyl groupafter 10 h reaction with various amounts of $KMnO_4$: a, 0.026 mphr; b, 0.044 mphr; c, 0.075 mphr; d, 0.145 mphr; and e, degraded NR under similar conditions with 0.075 mphr $KMnO_4$. (B) Ratio of A_{1717}/A_{2962} to the C-H symmetrical stretching vibration of the degraded ENR with different amounts of $KMnO_4$.

^{1}H-NMR spectrum of ENR 25 and the degraded product are shown in Figure **4.39**. There are a number of new peaks: 0.85 ppm of terminal methyl group, 1.21 ppm (C***H*****$_3$**CHOH), 2.34 ppm (C***H*****$_2$**COOCH$_3$), 3.64 ppm (CH$_2$COOC***H*****$_3$**), 3.90ppm (C***H***OH). In addition, a very weak peak at 9.78 ppm could be related to aldehyde.

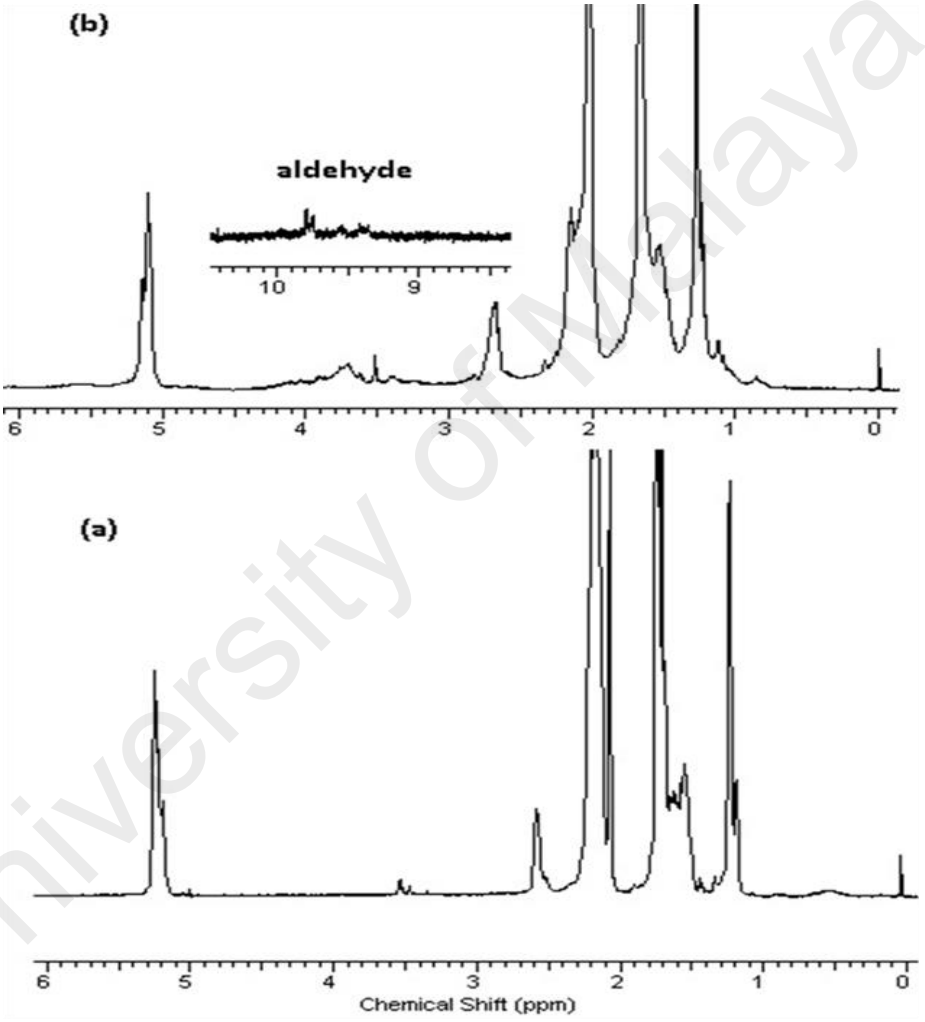


Figure 4.39: ^{1}H-NMR of (a) epoxidized natural rubber and (b)degraded ENR after reaction with 0.075 mphr $KMnO_4$.

The ratio of integration area of the signal at 5.11 ppm (olefinic methine proton) to 2.7 ppm (relating to epoxy methine proton) revealed a continuous decrease during

degradation with different amounts of $KMnO_4$ (Figure 4.40). As the mphr of potassium permanganate is increased the molecular weight of ENR decrease (Table 4.9).

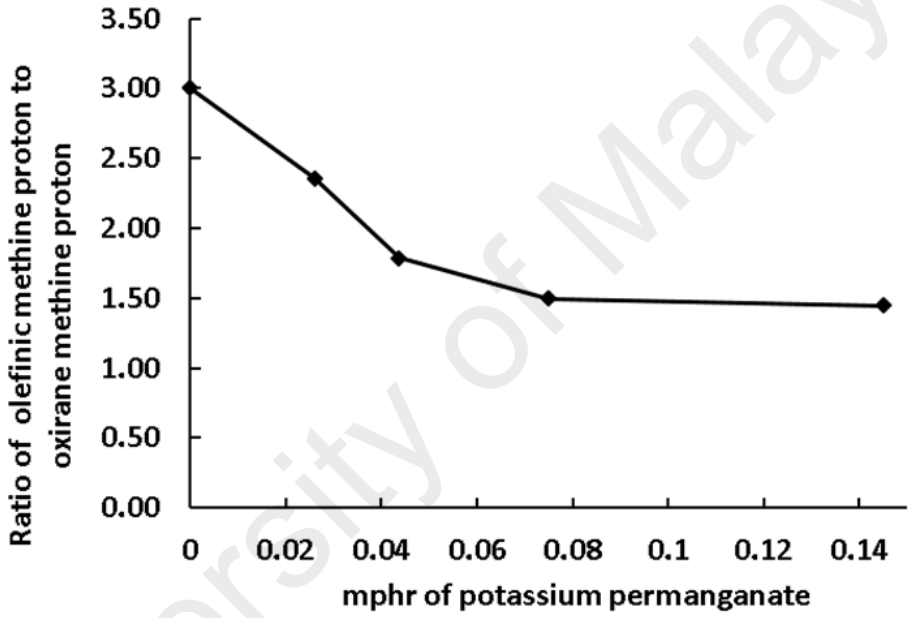


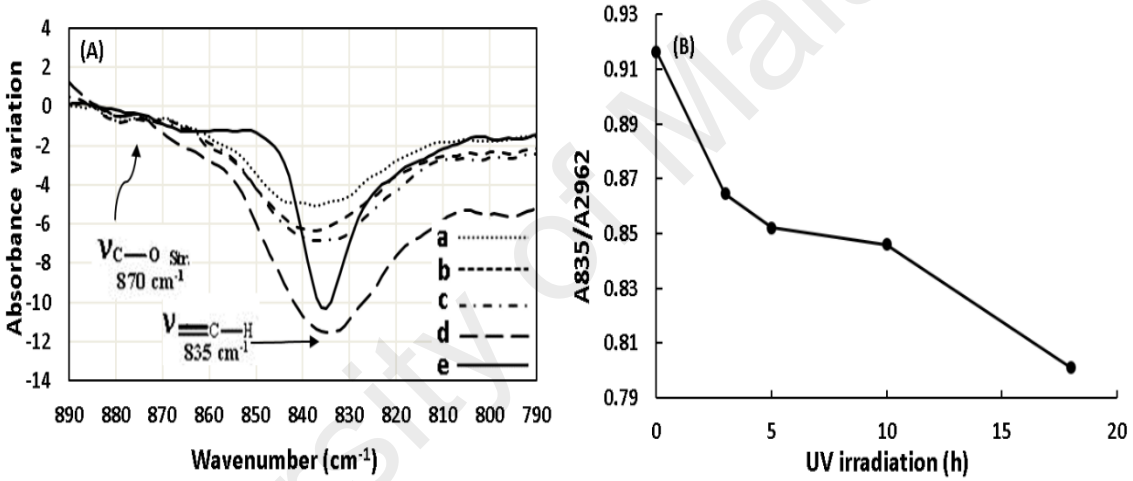
Figure 4.40: The ratio of the integration area of the signal at 5.11 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after degradation with different concentrations of potassium permanganate.

Table 4.9: Results of average molecular weight during degradation with $KMnO_4$ after 10 h of reaction.

Amount of $KMnO_4$ (mphr)	M_n	M_w
0	148000	696000
0.026	8880	205000
0.044	7320	71780
0.075	5950	51370
0.145	5470	31390

4.2.4 UV degradation method B

In the method B the intensity of irradiation was increased by approaching the UV lamp to the sample, which could accelerate the formation of free radicals. The effect of concentration was reported formerly by Ravindran et al. (1988). They have reported that by photo degradation of NR the extent of depolymerization was increased by decreasing of concentration of NR solution. The LENR obtained by method B is very similar to that obtained by method A (Section 4.1.4) but the efficiency of degradation in term of obtained molecular weight of LENR has been noticeably improved. The



subtracted IR spectra in the double bond and carbonyl region are shown in Figure 4.41 and Figure 4.42. In the carbonyl region, an increase in intensity of the peak at 1775 cm^{-1} related to lactone by increasing the radiation time is observed.

Figure 4.41: (A) Changes in absorbance of the double bond region(=C-H wagging) after different UV irradiation times: a, after 3 h; b, after 5 h; c, after 8 h; d, after 18 h; and e, degraded NR under the same condition after 10 h irradiation . (B) Ratio of A_{835}/A_{2962} in the degraded ENR during UV irradiation.

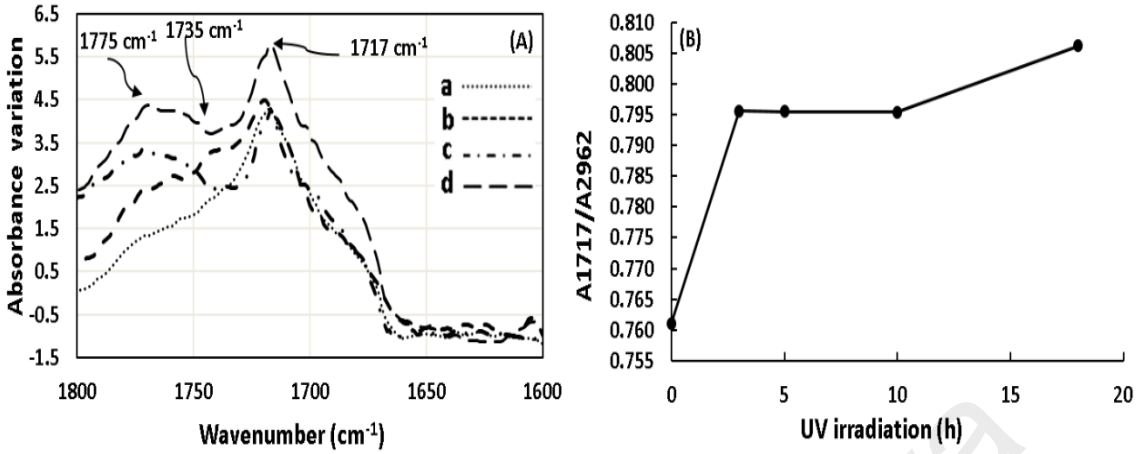
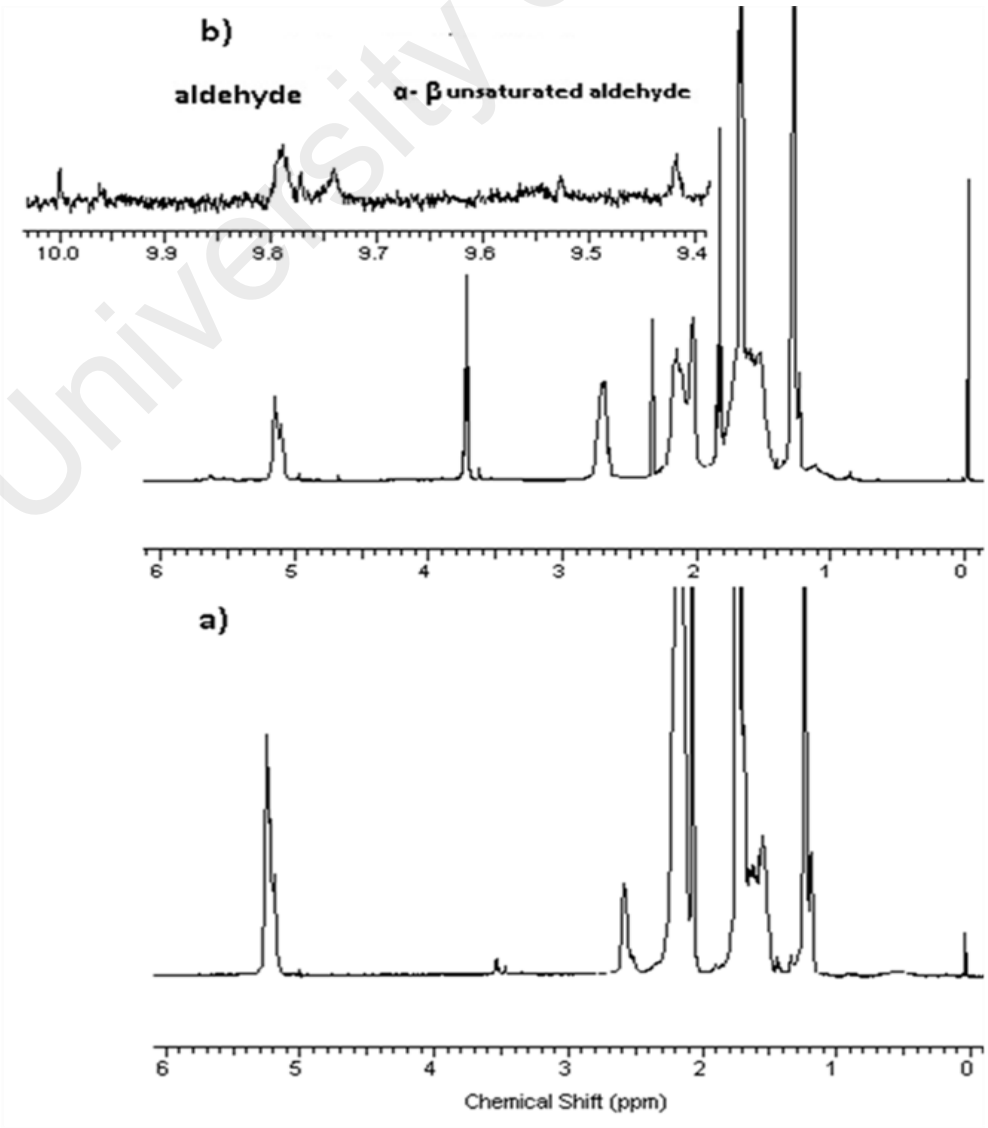


Figure 4.42: (A) Changes in absorbance of the carbonyl group after different UV irradiation times: a, after 3 h; b, after 5 h; c, after 10 h; d, after 18 h; and e, degraded NR under the same condition after 10 h irradiation. (B) Ratio of A_{1717}/A_{2962} in the degraded ENR during UV irradiation.

The NMR spectrum (Figure 4 43) shows also the creation of hydrofuranic structure as was observed before (Section 4.1.4). Ratio of integration area of the signals at 5.11 ppm to 2.7 ppm illustrated in Figure 4 44, shows that a reduction of double bond



occurred during of UV degradation. Both the number-average molecular weight (M_n) and the weight–average molecular weight (M_w) declined with increasing during UV irradiation related to the reaction time as is shown in Table 4.10.

Figure 4.43: (a) ^{1}H-NMR of epoxidized natural rubber; (b) degraded ENR by UV irradiation. The peaks at 1.83 ppm and 3.72 ppm could be related to hydrofuranic structure.

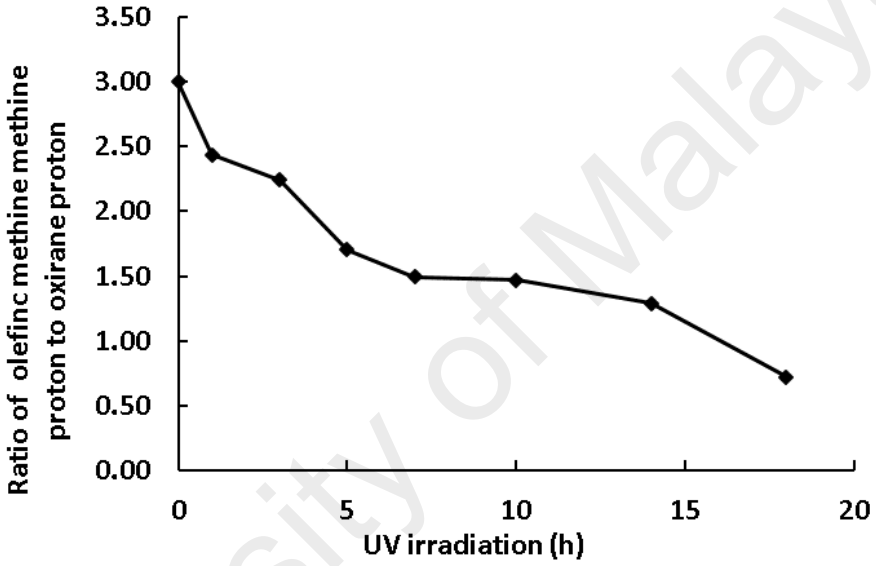


Figure 4.44: The ratio of the integration area of the signal at 5.11 ppm (olefinic methine proton) and 2.7 ppm (epoxy methine proton) after different UV irradiation times.

Table 4.10: Results of average molecular weight and polydispersity after UV irradiation.

Reaction time (h)	M_n	M_w	**PDI**
0	148391	695508	4.68
1	81043	227062	2.802
3	12457	56541	4.547
5	7463	31217	4.183
7	6128	29651	4.835
10	5563	20225	3.63
14	4427	18676	4.218
18	3588	16780	4.676

4.2.5 Comparison of the three methods

The LENR from different methods that have similar M_n were chosen for comparison. LENR degraded by (1) 0.026 mphr of H_5IO_6 has M_n about 7310, (2) 0.044 mphr $KMnO_4$ has a M_n of 7320 and (3) by UV-irradiation for 5 h has a M_n of 7460. Subtracted IR spectra in the carbonyl region show that in the UV degradation, carbonyl functional groups were formed less than the other methods as is shown in Figure 4 45. Prolonged UV radiation (Figure 4.2) and using higher amount of H_5IO_6 and $KMnO_4$ (Figure 4.33 and Figure 4.38) could lead to intense increase in carbonyl functional groups. Degradation by $KMnO_4$ at lowest concentration of 0.026 mphr produced only ketone at 1717 cm^{-1}, as is shown in Figure 4.38, but by increasing to 0.044 mphr, another peak appeared at 1735 cm^{-1} related to ester. Further of concentration above 0.044 mphr, peak at 1735 cm^{-1} has become stronger then the peak at 1717 cm^{-1}, this means more ester than ketone groups were generated. By contrast, degradation using H_5IO_6 has generated mainly ketone groups at 1717 cm^{-1}. UV irradiation above 5 h has produced another band at 1775 cm^{-1} beside 1717 $cm^{-1}$and 1735 cm^{-1}as is shown in Figure 4.42. The peak at 1775 cm^{-1} has been assigned to lactone (Piton & Rivaton, 1996).

The relationship between log M_n and the reaction time of different methods is illustrated in Figure 4.46. After one hour, M_n by UV photo oxidation is noticeably greater than the other methods. However, after the third hour, M_n was decreasing at similar rate as produced by 0.075 mphr of $KMnO_4$. The greatest degradation rate and the lowest M_n of LENR were achieved by the H_5IO_6 method.

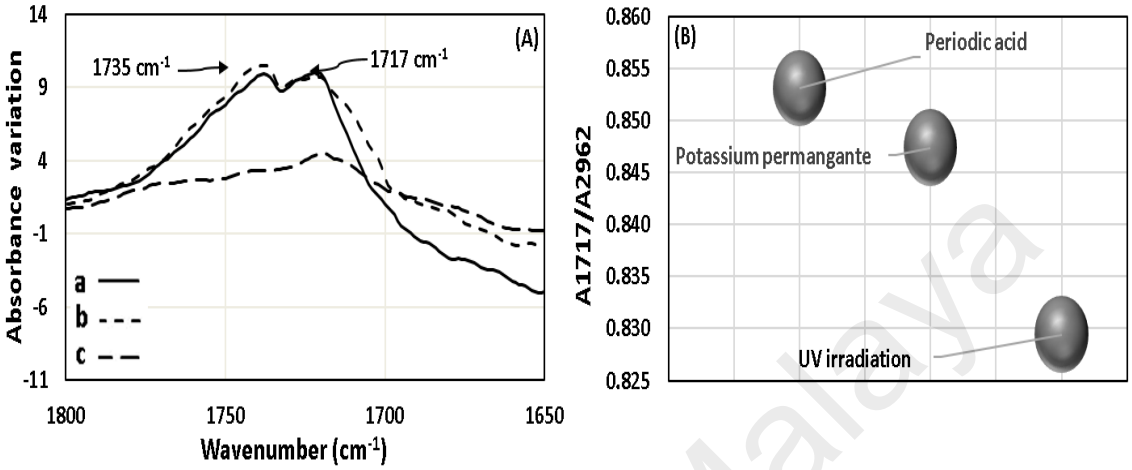


Figure 4.45: (A) Changes in absorbance of the carbonyl group. A comparison of three degradation methods: a, product of degradation by 0.026 mphr H_5IO_6; b, product of degradation by 0.044 mphr $KMnO_4$; c, degraded ENR 25 after 5 h UV irradiation. (B) Ratio of A_{1717}/A_{2962} of different degradation methods.

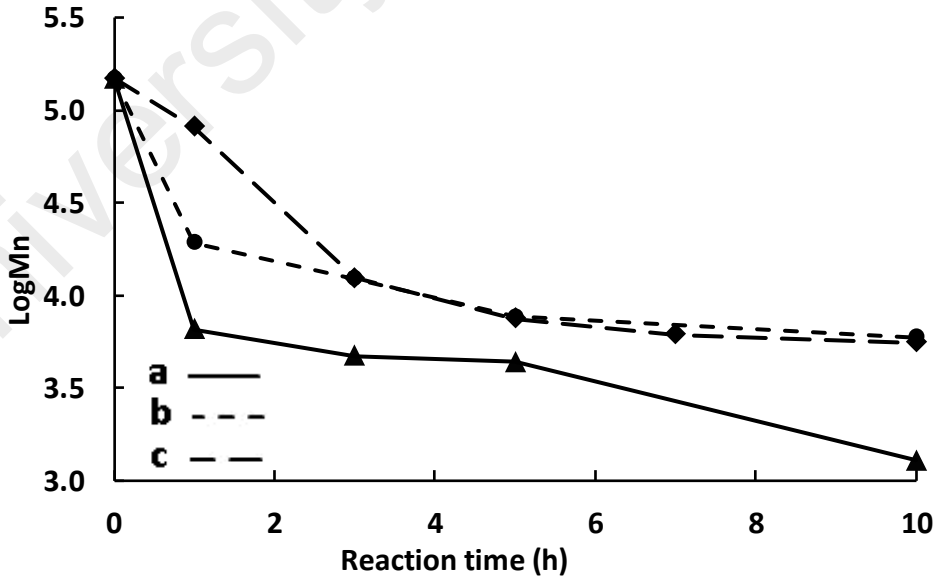


Figure 4.46: The decrease of log M_n during reaction time: a, degraded ENR by 0.075 mphr of H_5IO_6; b, degraded ENR by 0.075 mphr of $KMnO_4$; and c, degraded ENR by UV radiation.

The epoxy equivalent weight of LENR is calculated from titration with hydrobromic acid as discussed earlier is shown in Table 4.11. The double bond equivalent is determined based on the ratio of the integration area of epoxy methine proton to olefinic methine proton from NMR spectrum and the calculated epoxy content. Table 4.11 indicates that degradation with $KMnO_4$ involved both double bond and oxirane group but consumption of double bond is predominant. The ratio of olefinic methine proton to epoxy methine proton (Figure 4.40 and Figure 4.44) shows that degradation by $KMnO_4$ and UV irradiation occur predominantly through double bond as reflected by an increase in the ratio. The epoxide group is not noticeably affected by UV irradiation (Figure 4.41). Unstable terminal groups generated during chain scission could recombine leading to a rise in molecular weight. Thus, there is a competition between chain cleavage and cross linking reaction (Tangpakdee et al., 1998). The results of Table 4.11 show that the LENR from H_5IO_6 could achieve the same M_n with less change of double bond and oxirane during degradation by H_5IO_6.

Table 4.11: Results of epoxy equivalent weight degraded ENR25 obtained by different degradation methods.

Sample	Reaction time (h)	Cocentration of reagent (mphr)	M_n	Epoxy equivalent weight (g/eq)	Double bond equivalent weight (g/eq)
ENR 25			148391	295	97
Degraded ENR25 with H_5IO_6	10	0.026	7307	308	132
Degraded ENR25 with $KMnO_4$	10	0.044	7324	458	256
Degraded ENR25 with UV radiation	5		7463	311	183

[1]Double bond equivalent weight is determined based on the ratio of the integration area of epoxy methine proton to olefinic methine proton from ^{1}H NMR spectrum and the calculated epoxy content.

Gillert-Ritoit et al. (2003) reported that H_5IO_6 could attack epoxide group of ENR faster than double bond (Gillier- Ritoit et al., 2003). In contrast, Phinyocheep et

al. (2005) reported that degradation by H_5IO_6 did not take place at oxirane group because they did not observe any decline in epoxy content. They postulated that the carbon double bond was first oxidized to vic diol which is cleaved by another H_5IO_6 molecule (Phinyocheep et al., 2005). The epoxide equivalent weight of LENR by different concentration of H_5IO_6 is presented in Table 4.12. The results of this study show that H_5IO_6 at lower concentration prefer to attack the double bond but by increasing the concentration the degradation process take place at the epoxide ring. As mentioned, Table 4.12 shows a rapid decrease in oxirane group by employing higher concentration of H_5IO_6. The first step for transformation of epoxide function to vic diol begins with the attack of H^+. Therefore, pH plays an important role in the mechanism of reaction.

Table 4.12: Results of epoxy equivalent weight of LENR obtained from reaction at 10 h with H_5IO_6 at different concentrations.

Reaction time (h)	**Concenteration of H_5IO_6 (mphr)**	M_n	**Epoxy equivalent weight (g/eq)**	**[1]Double bond equivalent weight (g/eq)**
0	0	148391	295	97
10	0.026	7307	308	132
10	0.044	3907	475	157
10	0.075	1281	2175	239
10	0.145	1269	3343	234

[1]Double bond equivalent weight is determined based on the ratio of the integration area of epoxy methine proton to olefinic methine proton from ^1H NMR spectrum and the calculated epoxy content.

At lower pH, degradation takes place at double bond which is three times greater in amount than oxirane ring in ENR 25 chain. The results of Table 4.12 shows that by increasing the concentration of H_5IO_6 would cause a drop in pH, and the degradation take place predominantly at the epoxide groups. A proposed mechanism is shown in

Figure 4.47 (Fainleib et al., 2013). In acidic condition as is reported before cyclization of ENR can occur. A proposed mechanism for cyclization of degraded ENR is illustrated in Figure 4.48 (Sakdapipanich et al., 2002) .The double bond of cyclized rubber shows a peak in ^{1}H-NMR at 5.32 ppm. When $KMnO_4$ reacts with a double bond in cold acidic condition cyclic manganate ester is formed (Dash et al., 2009). Cyclic manganate esters is not stable and could react with water to form alpha hydroxyl ketone or it can undergo a cyclic fragmentation process which results in cleavage of double bond as is shown in Figure 4.49 (Yan & Schwartz, 1999). UV irradiation creates free radicals that could attack double bonds to form unstable peroxy radicals in present of oxygen as is described in Section 4.1.5.

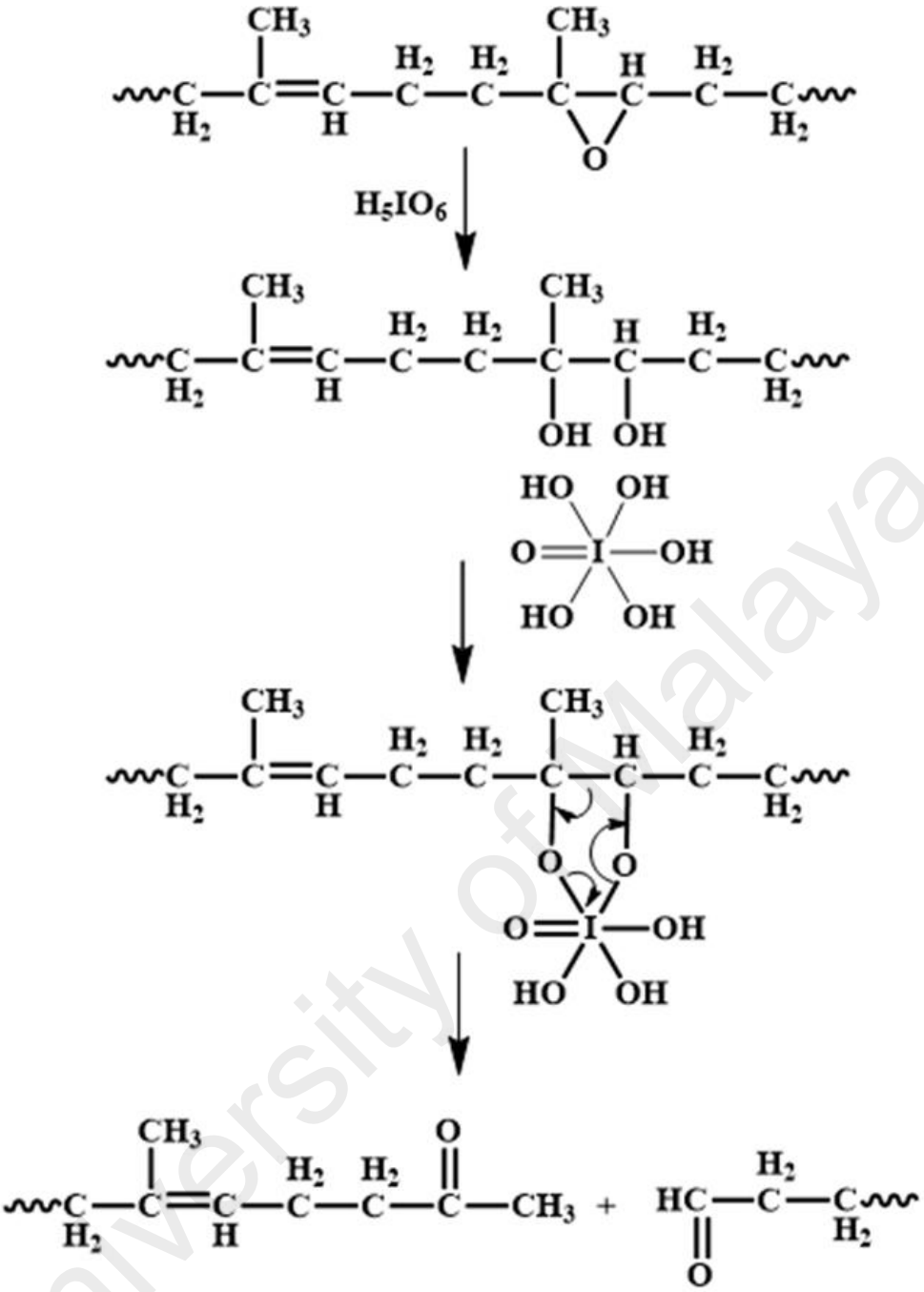


Figure 4.47: Proposed reaction pathway of degradation of ENR by higher amount of H_5IO_6.

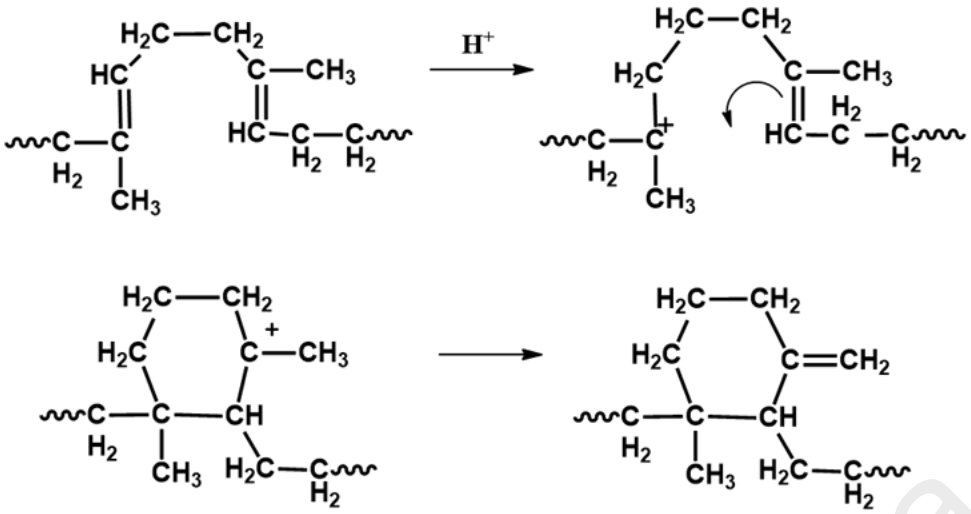


Figure 4.48: A suggested mechanism for cyclization of ENR in present of H_5IO_6.

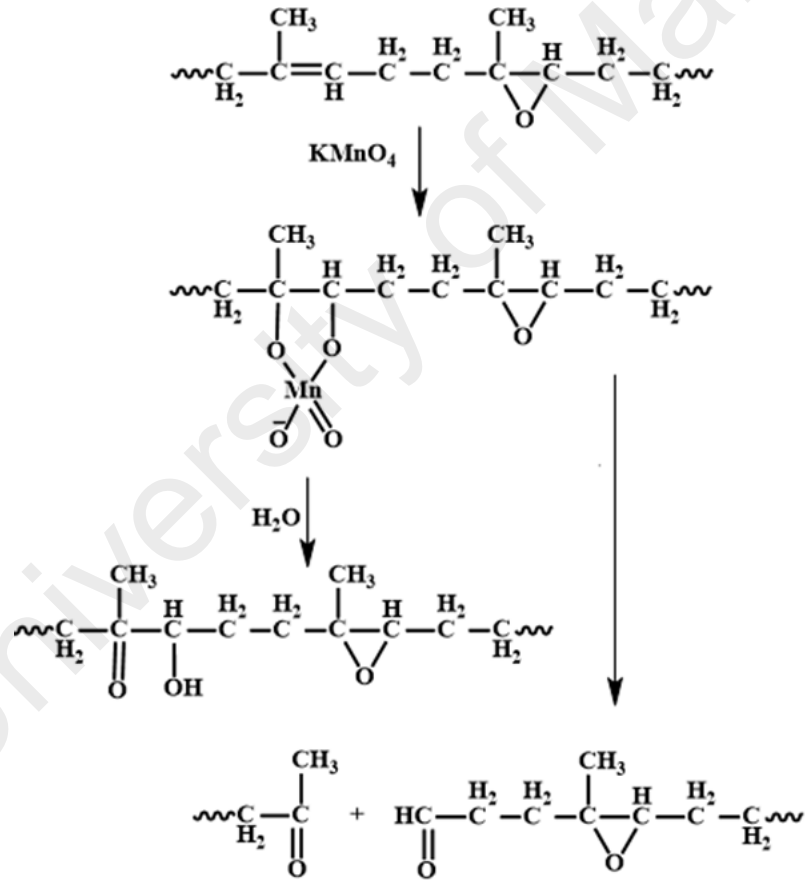
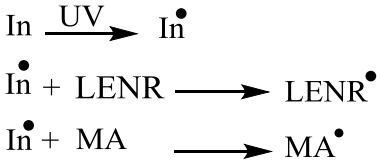


Figure 4.49: Presumed mechanism of degradation reaction of ENR in the presence of $KMnO_4$.

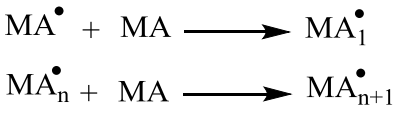
4.3 Preparation of coating based on LENR

LENR is a promising material for usage in coating applications. It has several properties required in coating industry including good solubility in organic solvents, good processability, good adhesion and wettability to various surfaces and outstanding elasticity (Jorge et al., 2010). Due to presence of oxirane group in the backbone of LENR it could be cured such as epoxy resin with an amine hardener. For this purpose, LENR suffers from some drawbacks, including low T_g and incompatibility with most of the hardeners used for curing of epoxy resin at room temperature. One way to overcome this problem is by grafting methyl methacrylate onto LENR. Graft copolymerization of NR and ENR has been done under different medium such as solution, latex and monomer media. Graft copolymerization on rubber is initiated by attack of free radical to the α methylene hydrogen atom (Arayapranee et al., 2002) . There are various methods to generate free radicals such as thermal decomposition of peroxides, persulfate dissociation, photo initiation or electron beam radiation. The graft copolymerization with electron beam does not need any photo initiator, because the bombardment of high energy electrons produce enough free radicals to push up graft polymerization. In this work, UV radiation is used to generate the free radicals. To accelerate the radical formation through UV radiation photo initiator is used to speed up free radical formation. The proposed mechanism is shown below in which MA, LENR and In indicate methyl methacrylate, liquid epoxidized natural rubber and initiator respectively:

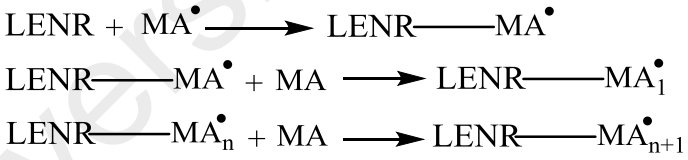


1) Initiation:

2) Propagation:

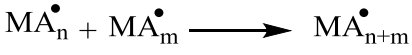


Homo polymerization:

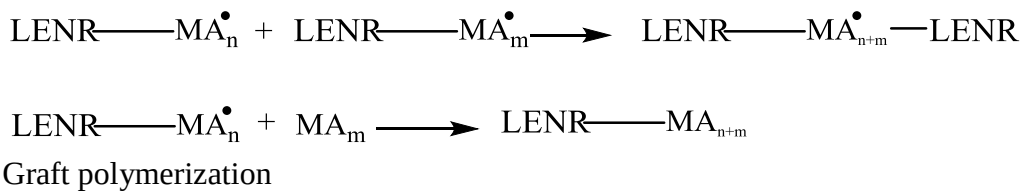


Graft polymerization:

3) Termination:



Homo polymerization



Graft polymerization

The rate of radical formation or the concentration of free radicals in the reaction medium will predominate graft polymerization to homo polymerization or vice versa. The grafting efficiency and conversion of methyl methacrylate are calculated as follows (Moolsin & Robishaw, 2011):

$$\text{Grafting efficiency } (\%) = \frac{(\text{weight of PMMA grafted})}{(\text{weight of PMMA grafted}) + (\text{weight of PMMA homopolymer})} x100$$

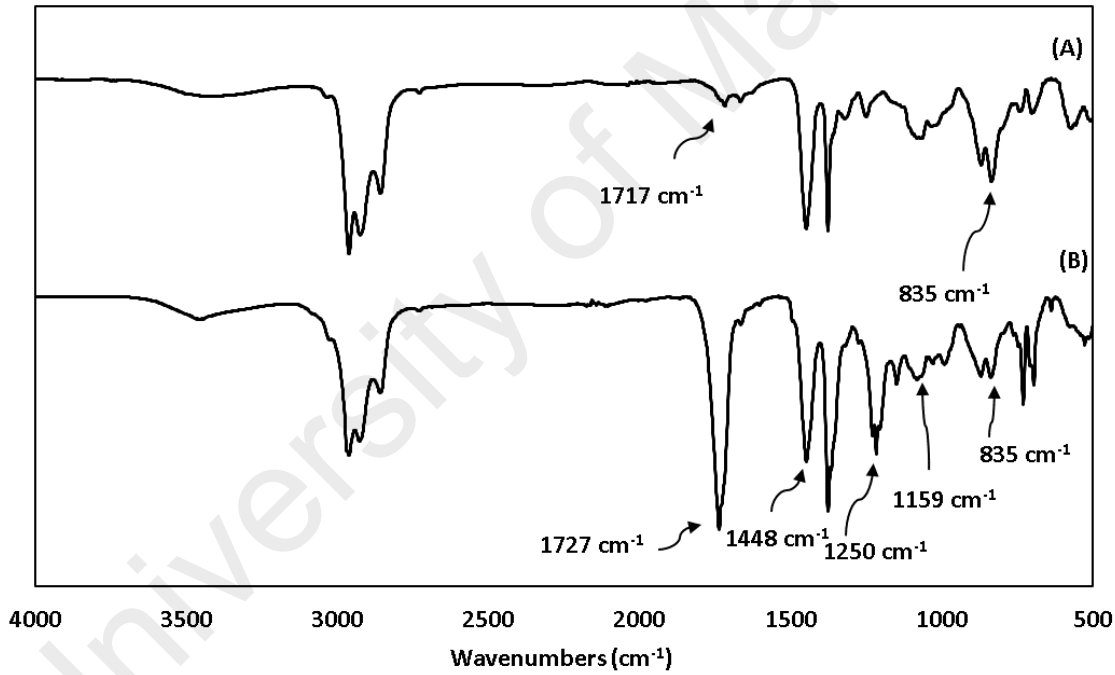
$$\text{Conversion } (\%) = \frac{(\text{weight of PMMA grafted}) + (\text{weight of PMMA homopolymer})}{(\text{weight of methyl methacrylate monomer})} x100$$

Methyl methacrylate was grafted onto LENR, obtained from UV photo oxidation method, with M_n of 11485 after 6h radiation which is coded LENR6 (Table 4.6). Graft copolymerization was done by using three different amounts of initiator concentration as is shown in Table 4.13. The products of graft copolymerization with different initiator concentrations are coded as GLENR1, GLENR2 and GLENR3 (Table 4.13). The amount of initiator used has an effect onto the grafting efficiency. By increasing in the initiator concentration more free radicals could be generated which will increase the grafting efficiency. Using higher concentration of initiator leads to formation of excessive radicals which could react together and so speed up the termination reaction. Meanwhile a decrease in grafting efficiency could be observed if homopolymerization is preferred to graft copolymerization.

Table 4.13: Effect of initiator concentration on graft copolymerization.

Sample	LENR (g)	MMA (g)	Benzophenon (g)	Grafting efficiency (%)	Conversion (%)
GLENR1	50	40	0.25	60.81	74
GLENR2	50	40	0.42	68.18	77
GLENR3	50	40	0.57	63.25	83

The IR spectrum shows a dramatic decrease in peak at 835 cm^{-1} which is related to double bond (Figure 4.50). The band at 1159 cm^{-1} can be attributed to the stretching vibration of the O-CH_3 group of methyl methacrylate. The band at 1250 cm^{-1} can be assigned to the –C-O-C- bond stretching vibration of methoxy and adjacent carbonyl group of methyl methacrylate. A very intense peak appears at 1727 cm^{-1} which could be related to ester functional group of methyl methacrylate. The carbonyl group of LENR6 is merged with this peak. The α-methylenic hydrogen atom in LENR is the most active site for graft copolymerization therefore, a decrease in the absorption band at 1448 cm^{-1} related to CH_2 (deformation) could be observed. On the other side a decrease in band at



835 cm^{-1} attributed to double bond shows that a part of graft copolymerization has been ocurred by direct attack to double bond.

Figure 4.50: FT-IR spectra of (A) LENR6 and (B) LENR-*graft*-MMA (GLENR2).

After graft copolymerization, additional peaks (compared to LENR6) appear in ^{1}H-NMR spectrum of LENR-graft-PMMA. Peak with great intensity at 3.68 ppm which could assign to methoxy proton of methyl methacrylate (-CH_2 $C(CH_3)(CO)OCH_3$) and another peak appears at to 2.29 ppm which is related to methylene group of methyl methacrylate (-$CH_2C(CH_3)(CO)OCH_3$) (Figure 4.51). DSC thermograms show a little positive shift in T_g of LENR compared to ENR 25. The increase in the T_g is due to appearance of polar groups in the backbone of the LENR during degradation process as described before. LENR-*graft*-PMMA also shows a great increase in T_g (42ºC), because incorporation of hard segments of PMMA onto LENR which improves hardness, T_g and lowers the modulus of the rubber (Dafader et al., 2006).

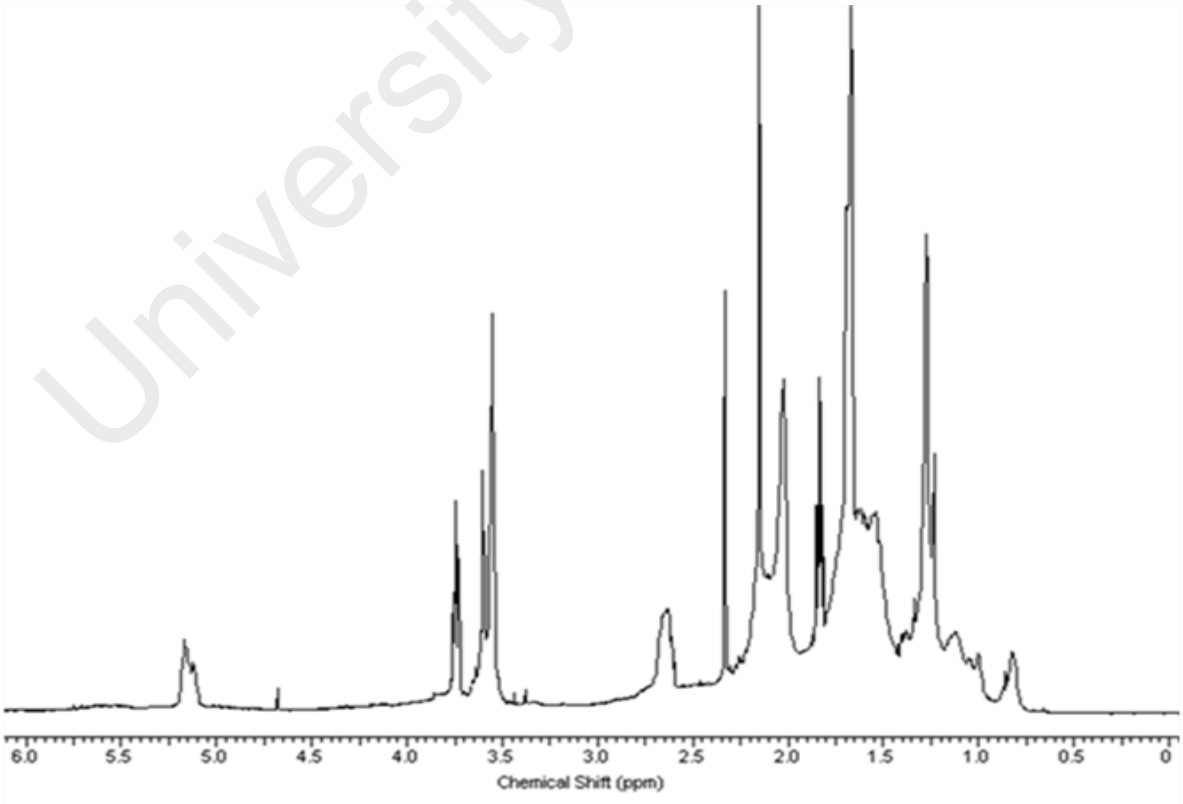


Figure 4.51: [1] H-NMR spectrum of the LENR-g-PMMA (GLENR2).

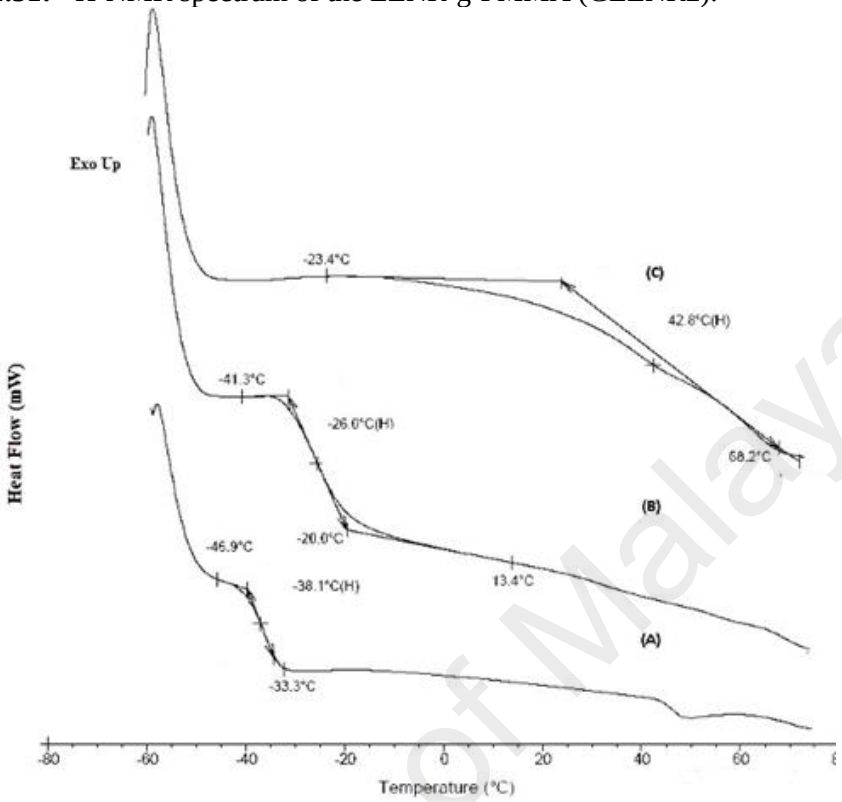


Figure 4.52: DSC curves of (A) ENR, (B) LENR6 and (C) LENR-*graft*-PMMA (GLENR2).

Epoxy resins (oxirane functional group containing resins) could react with a various number of chemical species called curing agents. The grafted LENR (GLENR) contains oxirane groups. The epoxy equivalent of GLENR2 was determined with the method described in section 3.4.5. Grafted LENR is a thermoplastic resin and could be converted to an infusible thermoset network by using a curing agent. This process could enhance strength and the elastic property of the grafted rubber due to formation of three-dimensional network by cross linking. The reaction between epoxy resins and a multifunctional hardener (curing agent) is usually polyaddition copolymerization. Three samples were prepared by mixing of GLENR2 with three different hardeners in stochiometric amount including Aradure 943, Epikure F205 and hexamethylenediamine (HDMA). The coatings obtained from curing of GLENR2 by Aradure 943, Epikure

F205 and HDMA are coded as GLCO1, GLCO2 and GLCO3 respectively. GLCO1, GLCO2 and GLCO3 were applied on iron panels and after drying the film properties were investigated (section3.5.4). The performance of the coatings was assessed by several test methods. American Standard Testing Methods organization (ASTM) has established a variety of methods for testing of coating which are useful in evaluating the performance and failure of coating. Nevertheless, there is no fully reliable testing methods to assess the appearance and characteristic of coated products. Table 4.14 shows the physicochemical properties of the coatings based on grafted LENR cured with amine containing hardeners. The fastest curing time is observed by GLCO3 coating cured with HDMA. HDMA is an aliphatic polyamine, this type of amine react very fast at ambient temperature with oxirane group. Aliphatic polyamines are very susceptible to blushing problem which is caused by reaction between amines, CO_2 and moisture. The appearance of the film cured with HDMA was a little bit blushed and hazed. The surface of dried film with HDMA was also not uniform. This could be caused by partial incompatibility of the resin and hardener. Epikure F205 is a cycloaliphatic amine and the obtained film was cured faster than the coating acquired by curing with Aradure 943. The appearances of GLCO1 and GLCO2 coatings were transparent and glossy.

Table 4.14: Chemical and physical properties of the coating materials.

Physicochemical properties/Epoxy coatings		**GLCO1**	**GLCO2**	**GLCO3**
	Testing methods/Type of Hardeners	**Aradure 943**	**Epikure F205**	**HMDA**
Drying time	Set to touch (h)	4	3.5	3
	Dry-to-touch (h)	25	21	19
Mechanical test	Pencil hardness	4H	5H	3H
	Adhesion test	5B	5B	3B
Water resistance	ASTM-D1647-89	3	2	4
Alkali resistance	0.1 M NaOH	4	4	6

Note-Water and alkali resistance behaviour: 1, unaffected; 2, slightly whitening; 3, heavily whitening;4, slightly shrinkage; 5, film soften; 6, film lift out

Hardness of a coating is defined as the capacity of a coating to resist to permanent or temporary deformation, damage, or penetration by hard object. Deformation of a coating implies mutual displacement and interchange of chain segment, therefore cross-linking density, entanglement, crystallinity and molecular structure of the resin of the coating has a noticeable effect on the hardness of the film (Fink-Jensen, 1965). The resistance of a coating against deformation decreases by increasing layer thickness; therefore, is very important to measure the thickness before testing the hardness of the film. The scratch hardness was determined by pencil hardness test. The results show that GLCO2 coating has the highest pencil hardness. This could be explained by presence of rigid cyclic structure of Epikure F205 (cycloaliphatic amine) in the network formation of the dried film. Adhesion and cohesion are two main factors which affect noticeably on durability and performance of a coating. Cohesion is measured by elongation test and is defined as inner strength of a material which is provided by the bonding force between the various molecules of the coating film. Adhesion could be defined as strength of bonds between the coating material and the substrate. There are different kinds of bonding forces such as covalent, metallic, hydrogen bonding, dispersion dipole and induction. Adhesion to the substrate begins with interfacial molecular contact by wetting process. A fluid such as coating is able to wet a surface (substrate) if it has a lower surface tension than substrate. After wetting, by penetrating of coating molecules across the interface, interfacial bonds between film and substrate are formed. LENR has low surface tension which is necessary for proper wettability of substrate. Presence of polar groups in methyl methacrylate and creation of hydroxyl group by ring opening of epoxide could provide an appropriate adhesion to iron substrate. Therefore, good adhesion is observed by GLCO1 and GLCO2 coatings. Incompatibility between resin and hardener in coating mixture affects the wetting process which could cause some decrease in adhesion to the

substrate as is observed by GLCO3 coating. Aliphatic polyamine molecule consists of two parts including amine functional group which has high polarity and a hydrocarbon part that is almost non-polar and hydrophobic, therefore by increasing of H active equivalent weight of hardener a rise in weight percentage of nonpolar group is expected. Increasing of non-polarity and hydrophobicity could improve the water impermeability. H active equivalent weight of HDMA and Epikure F205 are respectively 29 (g/eq) and 104 (g/eq). Consequently, a better water resistant was seen by GLCO2. Furthermore, a non-uniformity in film formation that was observed by GLCO3 could increase the water permeability and worsen the water resistance. Aradure 943 is an amine adduct hardener; this means that a little part of amine group has been reacted with oxirane group to increase the molecular weight and enhance the compatibility of hardener but Aradure 943 has still a low H active equivalent weight (38 g/eq), which could explain the lower water resistance of GLCO1 compared to GLCO2 coating cured with Epikure F205. Pendant hydroxyl group generated by curing reaction and polar groups present in MMA mostly provide the adhesion to the substrate. The ester groups in MMA are not resistant towards alkali. Hydrolysis of ester linkage is catalysed by alkali, therefore all of the coatings showed weak alkali resistance. FTIR spectra of GLENR. GLCO1, GLCO2 and GLCO3 are shown in Figure 4.53. FTIR spectra of coating samples show a noticeably decrease in absorption band at 870 cm^{-1}. This peak is attributed to the stretching vibration of oxirane ring. This observation implies that ring opening of oxirane group has been occurred during curing reactions.

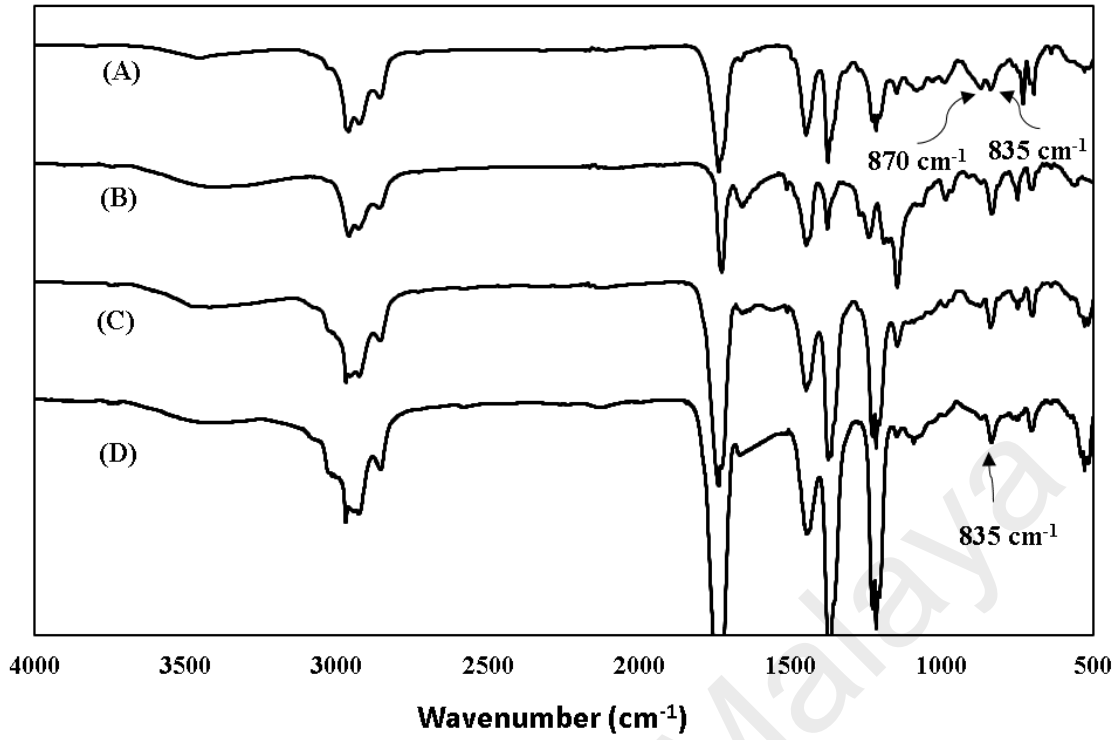


Figure 4.53: FTIR spectra of (A) GLENR, (B) GLCO1, (C) GLCO2, (D) GLCO3.

CHAPTER 5: CONCLUSION AND FURTHER WORK

5.1 Conclusions

Liquid epoxidized natural rubber (LENR) was successfully prepared by 5 different methods including (i) mechanical milling, (ii) degradation initiated by potassium peroxodisulfate (iii) photo-oxidation initiated by ultra violet (iv) oxidative degradation by periodic acid, (v) oxidative degradation using potassium permanganate.

The first three methods degraded ENR through radical mechanism. The products of these three methods were compared together. In all three methods, a decrease in double bond intensity is observed, but only in degradation with roll mill is there no linear relation between degradation degree and decrease of double bond. It could imply that generated radicals prefer to abstract an allylic hydrogen rather than add to the double bond. The comparison of the degradation products showed that UV degradation induced more carbonyl and hydroxyl group to the backbone of the ENR; therefore, its product has more saturated and less double bond compared to other two methods. In all these three methods ketone, aldehyde, ester and lactone were produced. NMR spectrum showed that hydrofuranic structure is the main product of UV degradation, which was not formed in reaction with $K_2S_2O_8$ and mastication. Depending on time, better yield was observed by UV degradation but increase of oxygen concentration did not enhance the efficiency in this method. An increase in oxygen concentration in UV degradation can lead to higher generation of free radicals which prevail cross linking reaction over degradation, therefore LENR with higher M_n was obtained. Decreasing of concentration

of ENR solution and increasing of intensity of irradiation in UV photo oxidation method, enhanced noticeably the efficiency of UV degradation.

The last two methods including degradation by H_5IO_6, and degradation using $KMnO_4$ generate LENR by oxidative degradation. LENR obtained from these methods was characterized and compared with LENR acquired by UV photo oxidation method. Degradation of ENR by $KMnO_4$ and UV irradiation continue mostly by attack via double bond, therefore a decrease in the ratio peak areas of olefinic methine proton to epoxy methine proton was observed. The results of oxirane group titration showed that degradation with periodic acid could take place at epoxide or via double bond group. At concentration of above 0.044 mol H_5IO_6, per hundred grams of rubber (mphr) degradation occurred by ring opening of oxirane group. FTIR and NMR results showed that LENR obtained by H_5IO_6 has more ketone groups while the LENR from degradation by $KMnO_4$ has more ester groups. Cyclization of isoprene unit was only observed during the degradation by H_5IO_6. Among these three methods, H_5IO_6 achieved the fastest rate of degradation and lowest M_n under comparable conditions.

Comparing of LENR obtained by these five methods shows:

1) In term of molecular weight oxidative degradation by H_5IO_6 and $KMnO_4$ are more effective than radical degradation.

2) LENR acquired by oxidative degradation methods has more polar carbonyl and ester group according to greater increase in intensity of absorption in carbonyl region in FTIR spectra.

3) Regarding to NMR spectrum in degradation by H_5IO_6, the diversity of carbonyl and hydroxyl group generated on the backbone of LENR was greater than other methods.

4) An increase in the ratio peak areas of olefinic methine proton to epoxy methine proton was observed only by degradation using H_5IO_6, which implies that degradation by H_5IO_6 occurs predominantly through oxirane group.

5) Mastication with two roll mill produced LENR with greatest degree of unsaturation and less amounts of polar groups; therefore, the chemical structure of LENR is more similar to ENR in comparison with other methods.

To improve the overall properties of LENR, methyl methacrylate was graft copolymerized onto LENR. Graft copolymerization was successfully done using UV radiation for formation of free radicals. To speed up free radical formation photo initiator, benzophenone, was used in different concentration. The amount of initiator used has an effect onto the grafting efficiency. By increasing in the initiator concentration an increase in the grafting efficiency was observed. Using a higher concentration of initiator speeds up the termination reaction. Meanwhile a decrease in grafting efficiency could be observed if homopolymerization is preferred to graft copolymerization. The best grafting efficiency was achieved by using 0.84 phr of benzophenone. Graft copolymerization on rubber is initiated by attack of free radical to the α methylene hydrogen atom, on the other side a decrease in band at 835 cm^{-1} attributed to double bond showed that a part of graft copolymerization has been occurred by direct attack to double bond. DSC thermograms showed a little positive shift in T_g of LENR compared to ENR 25. LENR-*graft*-PMMA showed a great increase in T_g (42ºC), because incorporation of hard segments of PMMA onto LENR. The graft

copolymerization improved the compatibility and mixability of LENR-graft-PMMA towards polar curing agents. LENR-*graft*-PMMA was mixed with three different kinds of hardeners including Aradure 943, Epikure F205 and hexamethylenediamine. The mixture was applied as coating on iron plate. The FTIR spectra of the coatings revealed a noticeable decrease in absorption band at 870 cm^{-1}which implies oxirane ring opening by curing reaction. The best chemical and physical properties were observed by the coating cured with Epikure F 205 (cycloaliphatic amine). Linear aliphatic amine containing short alkyl chain such as HMDA was not totally compatible with GLENR and the appearance of the film was a little bit blushed and hazed. Furthermore, the surface of dried film with HDMA was not uniform.

5.2 Suggestion for further research

This research has presented the groundwork for preparing epoxy resin for coating based on LENR as an environmentally friendly material. There are many reaction possibilities that can be used in improving this research. Epoxy resins are very reactive and could react with several different hardeners such as aliphatic amines, aromatic amines, polycarboxylic acids, polycarboxylic anhydrides, phenol-formaldehyde resins, amino-formaldehyde resins and mercaptans and so on, this makes them very versatile polymers to produce a broad range of coating materials with different properties. Another interesting prospect is to study the effect of other types of monomer grafted onto LENR. For example, grafting of 2-hydroxyethyl methacrylate onto LENR or LNR could improve the adhesion to substrate due to presence of hydroxyl groups and the resin has also the capability to be cured with different kinds of diisocyanates.

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LIST OF ISI PUBLICATIONS AND PRESENTATIONS

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